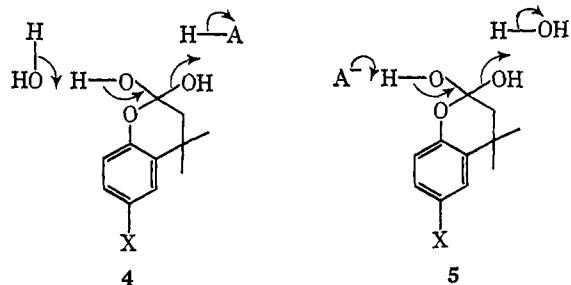


value of  $\rho$ , obtained for general base catalysis (Table II), is in accord with these considerations. The proposed mechanisms are supported further by the values of the solvent deuterium isotope effects. The magnitudes of the entropies of activation for hydronium ion catalysis ( $-20$  eu) and for general acid-base catalysis (*ca.*  $-30$  eu) suggest the additional participation of a molecule of water in each case.



Although numerous examples exist of general acid or general base catalysis of reactions of carboxylic acid derivatives,<sup>7</sup> concurrent catalysis by both species is more commonly known at the aldehyde level of oxidation, where tetrahedral intermediates are significantly more stable.<sup>8</sup> An early study of the esterification of acetic acid in methanol has provided the only data suggestive of general acid catalysis of such a reaction.<sup>9</sup> To our knowledge, the lactonizations of **1**, **2**, and **3** constitute the first examples of concurrent general acid and general base catalyzed esterifications.

(7) S. L. Johnson, *Advan. Phys. Org. Chem.*, **5**, 237 (1967).

(8) W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964).

(9) A. C. Rolfe and C. N. Hinshelwood, *Trans. Faraday Soc.*, **30**, 935 (1934).

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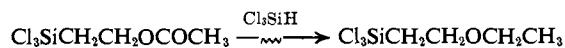
National Institute of Arthritis and Metabolic Diseases  
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Received June 9, 1969

### A Novel $\gamma$ -Induced Reduction with Trichlorosilane. Dialkyl Ether from Alkyl Aliphatic Carboxylate

Sir:

In the course of our study<sup>1</sup> on the  $\gamma$ -induced addition of trichlorosilane to vinyl acetate, we have found that the 1:1 adduct (2-trichlorosilylethyl acetate) is reduced to 2-trichlorosilylethyl ethyl ether under the conditions used. This finding indicates the possibility that a car-



boxylic ester, in general, can be reduced to an ether, the carbonyl group being converted to methylene. Reported here are the scope and sequence of this novel reaction. A degassed mixture of alkyl aliphatic carboxylate and trichlorosilane (1:6 molar ratio) in a fused tube was subjected to  $\gamma$  irradiation of 9.6 MR at a dose rate of 0.6 MR/hr at room temperature. After the irradiated product was dissolved in carbon tetrachloride, the ether was identified and estimated by glpc (FID). The results are summarized in Table I. Under the same conditions, however, esters  $\text{RCOOR}'$  ( $\text{R} = \text{CH}_3$ ;  $\text{R}'$

(1) J. Tsurugi, R. Nakao, and T. Fukumoto, submitted for publication.

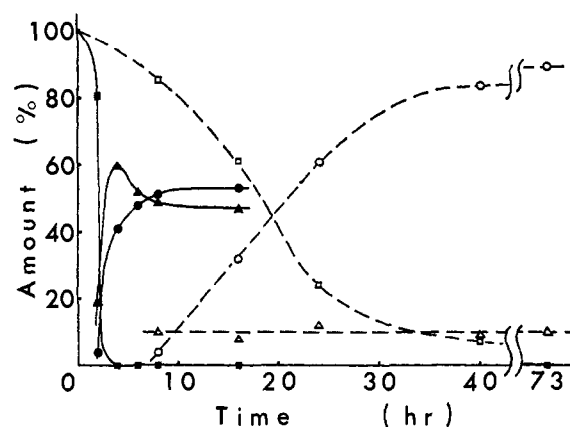


Figure 1. Reduction of ethyl acetate with trichlorosilane for various irradiation times: (---) 0.15 MR/hr; (—) 0.45 MR/hr; ( $\square$ ,  $\blacksquare$ ) [ether unchanged]; ( $\circ$ ,  $\bullet$ ) [ester produced]; ( $\triangle$ ,  $\blacktriangle$ )  $(100 - [\text{ester unchanged}]) - [\text{ether produced}]$ .

$\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5$ ; or  $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5$ ;  $\text{R}' = \text{C}_2\text{H}_5$ ) and ethyl thiolacetate ( $\text{CH}_3\text{COSC}_2\text{H}_5$ ) were recovered as such almost quantitatively after the irradiation. Therefore, it can be concluded that only alkyl aliphatic carboxylates can be reduced by this method.

Table I. Reduction of  $\text{RCOOR}'$  with Trichlorosilane under  $\gamma$  Irradiation

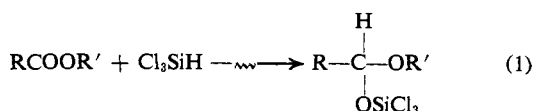
R	R'	Yield of $\text{RCH}_2\text{OR}'$ , %
H	<i>n</i> - $\text{C}_3\text{H}_7$	77
$\text{CH}_3$	$\text{C}_2\text{H}_5$	85
$\text{CH}_3$	<i>n</i> - $\text{C}_3\text{H}_7$	99
$\text{C}_2\text{H}_5$	$\text{CH}_3$	100
$\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_5$	100
$\text{C}_2\text{H}_5$	<i>n</i> - $\text{C}_3\text{H}_7$	96

To find a clue to the reaction scheme, a mixture of acetone and trichlorosilane (1:1 molar ratio) was irradiated (5.1 MR at 0.3 MR/hr) at room temperature. Distillation of the irradiated mixture gave isopropoxy-trichlorosilane [ $(\text{CH}_3)_2\text{CHOSiCl}_3$ ] in 81.5% yield: bp  $115^\circ$ ,  $n_{\text{D}}^{20}$  1.4050 (lit.<sup>2</sup> bp  $116^\circ$ ,  $n_{\text{D}}^{20}$  1.4045); nmr ( $\text{CCl}_4$ )  $\tau$  8.65 (d, 6,  $J = 11$  Hz,  $\text{CH}_3$ ), 5.46 (septet 1,  $J = 11$  Hz, CH). *Anal.* Calcd for  $\text{C}_3\text{H}_7\text{OSiCl}_3$ : Si, 14.51; Cl, 54.96. Found: Si, 14.87; Cl, 54.87. The same compound was reported<sup>2</sup> to be obtained by uv irradiation of the same mixture. Another series of experiments was run, in which a mixture of 1:2.2 molar ratio of ethyl acetate and trichlorosilane was irradiated for various time periods. Figure 1 shows that yield (*ca.* 50%) of the ether at a later stage using the higher dose rate (0.45 MR/hr) is lower than that (*ca.* 90%) under the lower dose rate (0.15 MR/hr) and that 2 *M* amounts of trichlorosilane is sufficient to reduce the ester with the lower dose rate. The calculated value,  $100 - [\text{ester unchanged}] (\%) - [\text{ether produced}] (\%)$ , signifies per cent sum of side product and intermediate. These

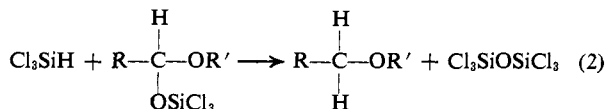
(2) (a) R. Calas and N. Duffaut, *Compt. Rend.*, **245**, 906 (1957). Many papers reported the addition of silanes to carbonyl groups, *i.e.*, trichlorosilane to acetaldehyde by uv,<sup>b</sup> trichlorosilane to dialkyl ketones by uv,<sup>c</sup> triethylsilane to ketones by zinc chloride,<sup>d</sup> and triphenylsilane to benzophenone by heat.<sup>e</sup> (b) R. Calas, N. Duffaut, and M. F. Menard, *Rev. Franc. Corps Gras*, **6**, 85 (1959); (c) ref 2a; (d) R. Calas, E. Frainet, and J. Bonastre, *Compt. Rend.*, **251**, 2987 (1960); (e) H. Gilman and D. Wittenberg, *J. Org. Chem.*, **23**, 501 (1958).

values (plotted in Figure 1) suggest the possible existence of an intermediate.

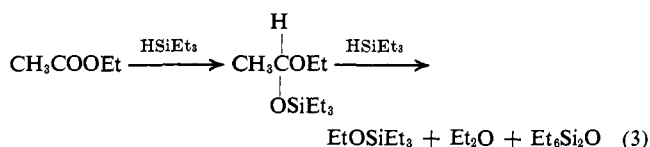
Analogy with the reaction of trichlorosilane with ketone suggests that the first step of the present reduction may be written as in eq 1. Although the inter-



mediate could not be isolated, it is considered to react further with another molecule of trichlorosilane (eq 2). The reduction<sup>3</sup> of ethyl acetate with triethyl-

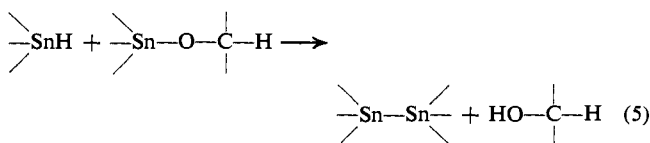
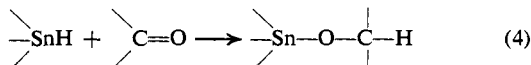


silane catalyzed by nickel chloride treated with triethylsilane proceeds as in eq 3. In this sequence, hexaethyl-



disiloxane corresponds to hexachlorodisiloxane in our reaction, but the yield of diethyl ether is much lower than ours, because of the side reaction producing triethylethoxysilane. In the present study, hexachlorodisiloxane expected in eq 2 was separated by distillation (8.3 g) from an irradiated (6.1 MR at 0.125 MR/hr) mixture of 70.4 g of ethyl acetate and 239 g of trichlorosilane (1:2.2 molar ratio) and identified by glpc after it was converted to hexamethoxydisiloxane.<sup>4</sup> The authentic hexamethoxydisiloxane was prepared *via* hexachlorodisiloxane, which was synthesized by partial hydrolysis of tetrachlorosilane.<sup>5</sup> Besides hexachlorodisiloxane, distillation of the irradiated mixture yielded tetrachlorosilane, 43 g (bp 58°, lit.<sup>6</sup> bp 58°), octachlorotrisiloxane, Cl<sub>3</sub>SiOSiCl<sub>2</sub>OSiCl<sub>3</sub>, 5.6 g (bp 75–77° (15 mm), lit.<sup>5</sup> bp 76° (15 mm)), and higher boiling fraction, 91.5 g, which was considered a mixture of higher siloxanes. Since Chambers and Wilkins<sup>6</sup> reported that hexachlorodisiloxane was decomposed to a mixture of higher chlorosiloxanes and tetrachlorosilane by heat, hexachlorodisiloxane produced in eq 2 might be rearranged also by  $\gamma$  irradiation.

Kuivila<sup>7</sup> proposed a free-radical mechanism for the addition of organotin hydride to carbonyl group, and proposed the sequence in eq 4 and 5 for the over-all reduction of carbonyl group to alcohol. In the present



(3) E. Frainnet and M. Paul, *Comp. Rend., Ser. C*, **265**, 1185 (1967).

(4) S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

(5) W. C. Schumb and A. J. Stevens, *J. Amer. Chem. Soc.*, **72**, 3178 (1950).

(6) D. W. S. Chambers and C. J. Wilkins, *J. Chem. Soc.*, 5088 (1960).

(7) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 70 (1964).

study eq 1 seems to proceed by a radical mechanism, because uv irradiation of a mixture of ethyl acetate and trichlorosilane confirms the formation of diethyl ether, although qualitatively.<sup>8</sup> The comparatively high *G* value of 435 which was calculated from the run for 24-hr irradiation under 0.15 MR/hr in Figure 1 suggests a radical-chain mechanism for eq 1. As mentioned above, RCOOR', either R or R' aryl, was not reduced by this method. The probable reason may consist in eq 1 not applying for esters of this type similarly to the case for ketone.<sup>2</sup> Our experiments also confirm that acetophenone and benzophenone were recovered almost quantitatively after  $\gamma$  irradiation (9.6 MR) of the mixture with trichlorosilane (1:6 molar ratio). The reason that when either R or R' was a benzyl group the reduction does not occur is obscure at present. Equation 2 seems to proceed without  $\gamma$  irradiation. Because of the affinity of Si for an O atom, disiloxane is formed instead of catenated compound as in the case of tin hydride.

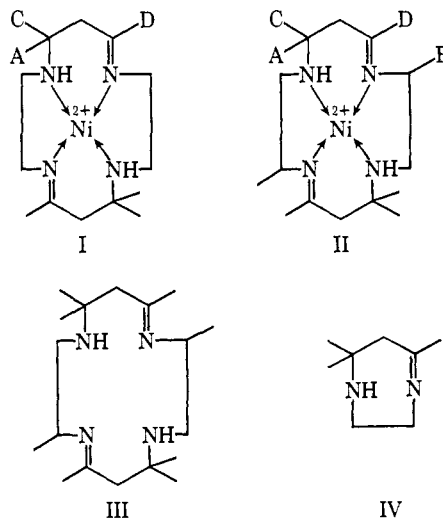
(8) Mechanistic study by uv irradiation is now carrying out at our laboratory.

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Received June 2, 1969

### Isomerism of Some Octamethyl-1,5,8,12-tetraazacyclotetradecadiene Complexes of Nickel(II) and Copper(II)

Sir:

Tris[( $\pm$ )-1,2-diaminopropane]nickel(II) perchlorate reacts with acetone to form two noninterconvertible isomeric octamethyl-1,5,8,12-tetraazacyclotetradecadienenickel(II) complexes.<sup>1</sup> The site of the isomerism was unknown, three possibilities being (i) the positions of the imino groups *cis* (1,11) or *trans* (1,8) with respect to the nickel ion, as observed for the hexamethyl analogs, *trans*, I, and *cis*, similarly formed with diaminoethane;<sup>2</sup> (ii) racemic or *meso* modifications associated with the two asymmetric carbon centers of the diaminopropane residues (any isomers associated



(1) M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1204 (1962).

(2) N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *ibid.*, **A**, 1015 (1966); M. F. Bailey and I. E. Maxwell, *Chem. Commun.*, 908 (1966); R. R. Ryan, B. T. Kilbourn, and J. D. Dunitz, *ibid.*, 910 (1966).