Journal of Organometallic Chemistry, 362 (1989) 31–35
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

γ-Ray-induced reduction of sterically hindered alkyl carboxylates with trichlorosilane in the presence of hydrogen chloride. Two-step mechanism for the formation of alkanes via the alkyl chloride

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(Received July 4th, 1988)

Abstract

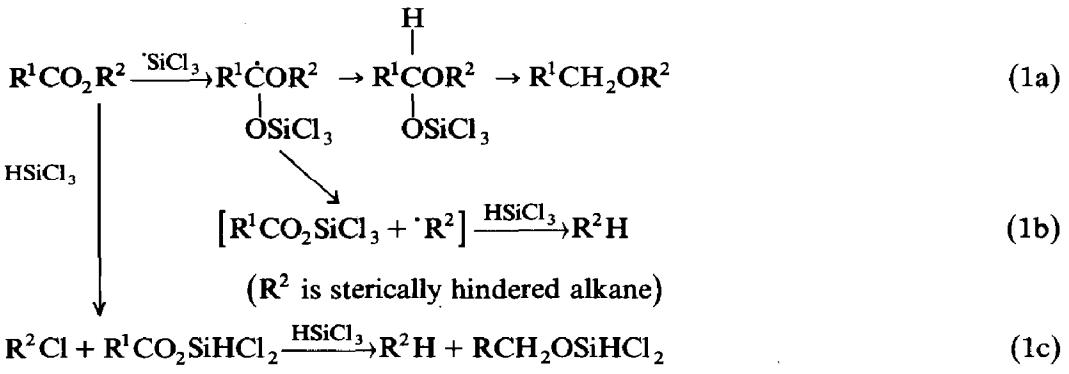
γ-Irradiation of a mixture of 1-adamantyl acetate and trichlorosilane (TCS) in the presence of hydrogen chloride yields adamantane. The first step of this reaction entails cleavage of the alkyl–oxygen bond by the action of HCl and TCS to give the alkyl chloride. The chloride, in the second step, is dechlorinated by TCS by a known, free-radical mechanism. t-Amyl and benzyl acetates react analogously to 1-adamantyl acetate in this system to give isopentane and toluene, whereas other primary and secondary alkyl derivatives produce the corresponding dialkyl ethers by a known, free-radical mechanism.

Introduction

Free-radical deoxygenation of alcohols via their carboxylates has been recognized as an important mean of modifying natural products. Many reducing agents have been reported for this purpose [1]. Trichlorosilane (TCS) is a novel and versatile reducing agent under free-radical reaction conditions [2–6]. When an alkyl carboxylate is subjected to a free-radical reaction with TCS, three different mechanisms, viz. **1a**, **1b** and **1c** in eq. 1 are possible. According to eq. 1a, the corresponding dialkyl ether is produced by a well-established sequence of free-radical chain reactions [2,3]. On the other hand, when the R^2 group is bulky, the corresponding alkane, R^2H, is formed, either via decomposition of the adduct radical (eq. 1b) [4] or via transient formation of R^2Cl (eq. 1c) [5]. A number of factors controlling the reaction path have been suggested [5,6], but in view of the versatility of the free-radical reduction using TCS, a more detailed study is necessary to obtain information on the controlling factors so that the optimal conditions for each reaction path can be found.

0022-328X/89/$03.50

We report here the mechanistic study on the γ-ray-induced reaction of alkyl carboxylates with TCS.



$$R^1CO_2R^2 \xrightarrow{{}^{\cdot}SiCl_3} R^1\dot{C}(OSiCl_3)OR^2 \rightarrow R^1CH(OSiCl_3)OR^2 \rightarrow R^1CH_2OR^2 \quad (1a)$$

$$HSiCl_3 \downarrow \qquad \searrow$$

$$[R^1CO_2SiCl_3 + {}^{\cdot}R^2] \xrightarrow{HSiCl_3} R^2H \quad (1b)$$

(R^2 is sterically hindered alkane)

$$R^2Cl + R^1CO_2SiHCl_2 \xrightarrow{HSiCl_3} R^2H + RCH_2OSiHCl_2 \quad (1c)$$

(R^2 is t-butyl)

Results and discussion

γ-Ray irradiation (dose 1.06 Mrad) of a mixture of 1-adamantyl acetate (ADA) and TCS (1/10) at room temperature gave exclusively 1-adamantyl ethyl ether and no adamantane(ADH) (Table 1). The reaction path followed here is solely 1a.

We have reported [5] that t-butyl carboxylate was converted into 2-chloro-2-methylpropane quantitatively when it was mixed with ten-fold amount of TCS at 40 °C. Temperature at which the reaction was run is critical.

In view of this, the effect of the temperature on the reaction of ADA with TCS was studied. As shown in Table 2, adamantyl chloride (ADCl) was produced in 4.9% yield at 60 °C after 7 h, which is poor when compared with the quantitative yield of 2-chloro-2-methylpropane [5] mentioned above, but this is probably because hyperconjugation by the three methyl groups in the t-butyl group facilitates breaking of the alkyl–oxygen bond [7]. In the presence of TCS, once the ADCl is formed, it is subsequently converted into ADH via a free-radical, such as that described in Table 1.

To obtain (ADH) by the reduction of ADA, alkyl–oxygen bond scission prior to a free-radical reaction must take place. Hydrogen iodide is known to cleave alkyl–oxygen bonds, but it can inhibit the subsequent radical reactions [8]. In view of this we examined the possibility of using hydrogen chloride as an alternative

Table 1

γ-Ray- and photo-induced reduction of 1-adamantyl acetate

$CH_3CO_2Ad + HSiCl_3$ (Ad = 1-adamantyl) →		$AdH + AdOC_2H_5$	
Molar Ratio	Method	Product Ratio	
1/10	γ-rays	0	100
1/10	γ-rays/60 °C	10	90
1/12	DTBPO/η^{p}	52	48 [a]

[a] Baldwin's result [4].

Table 2

Effects of the addition of hydrogen chloride and of the heating on the cleavage of 1-adamantyl acetate into 1-chloroadamantane

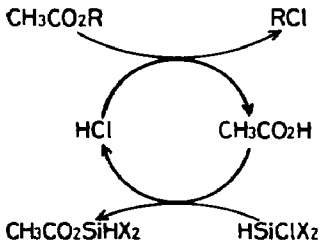
$CH_3CO_2Ad + HSiCl_3 \xrightarrow{HCl} AdCl$

(Ad = 1-Adamantyl)

Run	$\frac{[HSiCl_3]}{[Ester]}$	$\frac{[HCl]}{[Ester]}$	Temperature (°C)	Time (h)	AdCl (%)
1	10	0	5.6		0
2	10	0	60	7	4.9
3	12	0.5	r.t.		28.6
4	12	0.5	40	0.75	47.8
5	12	0.5	60	6	86

candidate for cleaving the alkyl-oxygen bond in ADA. Mixtures of ADA, TCS, and anhydrous hydrogen chloride were left to stand for a certain length of time at various temperatures, and ADCl was obtained as expected (Table 2). The results in Table 2 clearly indicate that either the addition of HCl, or heating the reaction mixture, increases the yield of ADCl.

Irradiation of a mixture containing the 86% yield of ADCl (entry 5) gave an 89% yield of ADH. Thus at concentrations of 0.5 mol or less relative to 1 mol of ADA, HCl does not interfere with the free-radical dechlorination reaction. The production of 2-chloro-2-methylpropane from t-butyl acetate without addition of HCl can also be understood in terms of the same reaction between t-butyl acetate and HCl, since TCS unavoidably contains a small amount of HCl *.



Scheme 1.

We conclude therefore, that the reaction to form an alkane from a corresponding alkyl carboxylate and TCS in the presence of HCl proceeds via two-step mechanism (Scheme 1); the HCl first reacts with alkyl carboxylate to yield the alkyl chloride and the carboxylic acid which subsequently reacts with chlorosilane to afford acetoxydichlorosilane and so regenerating HCl. The alkyl chloride thus produced is incorporated in the free-radical chain dechlorination reaction [6,9]. Acetoxydichlorosilane is finally reduced to ethoxydichlorosilane by eq. 1a.

Baldwin et al. [4] reported that photo-induced reduction of ADA in the presence of TCS gave equal amounts of ADH and 1-adamantylethyl ether (Table 1). The

* TCS is moisture-sensitive and can react with silanol groups in the glass wall of the vessel to produce hydrogen chloride.

Table 3

Reduction of alkyl acetates with trichlorosilane in the presence of hydrogen chloride

$$CH_3CO_2R + HSiCl_3 \xrightarrow[\gamma\text{-Rays}]{HCl} Rh + ROCH_2CH_3$$

Run	R	$\frac{[HSiCl_3]}{[Ester]}$	$\frac{[HCl]}{[Ester]}$	Dose (Mrad)	Temperature (°C)	RH (%)	$ROCH_2CH_3$ (%)
6	c-C_6H_{11}	10	1.6	16	r.t.	2.1	55.7
7	n-$C_{10}H_{21}$	7	1.6	20	125	1.6	90.
8	t-C_5H_{11}	6	1	2.3	r.t.	98	ND [a]
9	sec-C_4H_9	10	0.5	4	70	ND [a]	99
10	iso-C_3H_7	4	0.5	4	60	ND [a]	98
11	CH_2=$CHCH_2$	6	0.5	3	60	ND [a]	54.9
12	$CH_3COCH_2CH_2$	3	0.5	3	60	ND [a]	50.9
13	C_6H_5	5	2.5	2	125	ND [a]	1
14	$C_6H_5CH_2$	5.3	0.5	2	125	92	ND [a]
15	$C_6H_5CH_2CH_2$	6.8	0.75	2	125	24	49

[a] Not detected.

mechanism of this ADH formation was suggested as **1b** in eq. 1. In their experiments, however, the samples were irradiated at short distance (12 mm) by a 450-W medium pressure mercury lamp. Our experience using a similar lamp indicates that the temperature of the samples could have exceeded 60 °C. Furthermore, the photolysis of di-t-butyl peroxide under their experimental conditions might have yielded as much HCl as we used in this study *. Their reaction conditions may thus be regarded as being very similar to ours', entry 5 in Table 2 in which the formation of ADCl was facilitated.

We cannot conclusively rule out mechanism (1b) proposed by Baldwin et al. [4], but we suggest that at least part of the formation of ADH in their reactions can be accounted for in terms of the reactions depicted in Scheme 1.

To test the usefulness of this reaction as a means of deoxygenating alcohols via carboxylates, we carried out γ-induced reactions with various alkyl acetates in the presence of HCl. As shown in Table 3, t-amyl and benzyl acetates yielded quantitatively the corresponding alkanes, while primary and secondary alkyl acetates scarcely gave the alkanes, irrespective of the presence of hydrogen chloride [2]; dialkyl ethers were obtained in good yield. Phenylethyl acetate gave both products.

The present study has revealed that the key step of the γ-ray-induced reduction of alkyl carboxylate to alkane is the cleavage of the alkyl-oxygen bond in the presence of HCl and TCS. The reaction is only applicable to the reduction of t-alkyl, benzyl, and phenethyl acetates.

Experimental

Mass spectra were recorded on a Shimadzu LKB 9000 gas chromatograph-mass spectrometer. NMR spectra were obtained with a JEOL MN-100 spectrometer using

* On photolysis, di-t-butyl peroxide decomposes into two t-butoxy radicals which are efficient hydrogen abstractors producing t-butyl alcohol [10]. t-Butyl alcohol reacts with TCS yielding HCl. The amount of HCl produced in their experiment is not accurately known but it can be tentatively assumed as [HCl]/[substrate] > 0.5 because the reaction was started with [peroxide]/[substrate] = 0.5 [4].

tetramethylsilane as an internal standard. GLPC analyses were performed on Shimadzu GC-6AMPrTF using thermal conductivity and flame ionization detectors coupled with a Shimadzu Chromatopack C-R1A integrator. Glass columns (4 mm × 2 m) packed with 25% DC-200 or 30% SE 30 on Celite 545 were used. The amounts of HCl, CCl_4, tetramethylsilane and alkanes were measured on a Senson Pressure Transducer Model A coupled with a Sokken Model SPX-A amplifier which was attached to a vacuum line of known volume. γ-Rays were emissions from a 10 kCi ^{60}Co source. Samples were heated in an electric oven. TCS was distilled several times under vacuum after treatment with quinoline. ADA was prepared by a reported method [11]. 1-Adamantyl ethyl ether was isolated from a γ-irradiated mixture of ADA and TCS after careful hydrolysis with aqueous sodium hydroxide (NMR δ 1.06 (t, CH_3, J 6.2 Hz), δ 1.09–1.95 (m, adamantyl), δ 3.39 (q, CH_2, J 6.2) and mass spectrum, M^+ $m/z = 180$). Other reagents were commercial products and were used as received.

General procedure

Some ADA (ca. 1.5 mmol) and an appropriate cycloalkane as the internal standard for GLPC analysis, were put into a Pyrex tube which was then attached to a vacuum line. The sample was degassed by several freeze-and-thaw cycles, and TCS (ca. 15 mmol) was introduced. The sample tube was then sealed. It was irradiated by γ-rays at a dose rate of 1.6×10^5 rad, at a known temperature. The irradiated mixture was diluted with an appopriate solvent, and then subjected to GLPC analysis. Irradiations above room temperature or thermal reactions were carried out in an electric oven. The reaction products were identified from their GLPC retention times. The reactions of the other acetates with TCS were studied similarly.

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