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THE REACTION OF TRIS(TRIMETHYLSILYL)SILANE WITH ACID CHLORIDES

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Summary: Tris(trimethylsilyl)silane, in contrast with tributyltin hydride, reduces acid chlorides to the corresponding decarboxylated hydrocarbons via a free radical mechanism. This methodology could be a viable alternative to Barton's decarboxylation reaction.

Tributyltin hydride reacts spontaneously at ambient temperature with acid chlorides, RC(O)Cl, to form Bu_3SnCl, RCHO, $RC(O)OCH_2R$ and a number of minor products.[1] It is well-known that the majority of reactions involving tributyltin hydride occur via free radicals.[2] Ingold and coworkers[3] have shown, in disagreement with earlier conclusions,[4] that free radicals are not involved in such a spontaneous reaction. When free radicals are deliberately generated in the system, the nature of the products may be changed.[5] In fact, the reproducibility of the product distribution for the radical initiated reactions was relatively poor, the reason probably being that the free radical process and the spontaneous reaction occur together.

Although acid chlorides have not directly participated in the development of many methodologies in radical-based syntheses, a broad-based type of radical chemistry derived from the acyl derivatives of thiohydroxamic acids has been invented by Barton and coworkers.[6]

However, the reduction of acid chlorides under free radical conditions has been accomplished either by Pr_3SiH[7] or Cl_3SiH.[8] That is, tripropylsilane reacts with RCOCl in the presence of di-*tert*-butyl peroxide at 140-170°C to give the corresponding alkane RH in 50-70% yield when R is a primary or secondary alkyl group,[7] whereas the γ-ray induced reduction of acid chlorides with trichlorosilane at ambient temperature gives RH and/or RCH_2OSiCl_3 as final products in a ratio that depends on the nature of R.[8]

We have recently shown that tris(trimethylsilyl)silane is an attractive alternative to tributyltin hydride for the majority of its radical chain reactions.[9] The fact that some silanes do not react spontaneously with acid chlorides,[7,8] has persuaded us to undertake a study on the radical initiated reactions of $(Me_3Si)_3SiH$ with RCOCl. We report here our preliminary work on the reduction of acid chlorides via radicals.

A mixture of $(Me_3Si)_3SiH$, acid chloride and toluene as solvent was kept at ambient temperature for 72 hours and then heated at 80°C for 10 hours. Analysis by GC revealed the absence of new products. Therefore, no spontaneous reaction occurs between $(Me_3Si)_3SiH$ and acid chlorides under neutral conditions. On the other hand, when a radical initiator is introduced, a reaction takes place. Table I shows the reaction conditions and yields for the reduction of primary, secondary and tertiary acid chlorides to the corresponding hydrocarbons.[10]

Table I. Reduction of Acid Chlorides by Tris(trimethylsilyl)silane[a]

RCOCl	Initiator	T, °C	Yield RH (%)
$CH_3(CH_2)_{10}COCl$	$Me_3COOCMe_3$	165	87
c-$C_6H_{11}COCl$	AIBN	80	92
AdCOCl	AIBN	80	90

[a] In dodecane. [RCOCl]:[SiH] = 2:3.

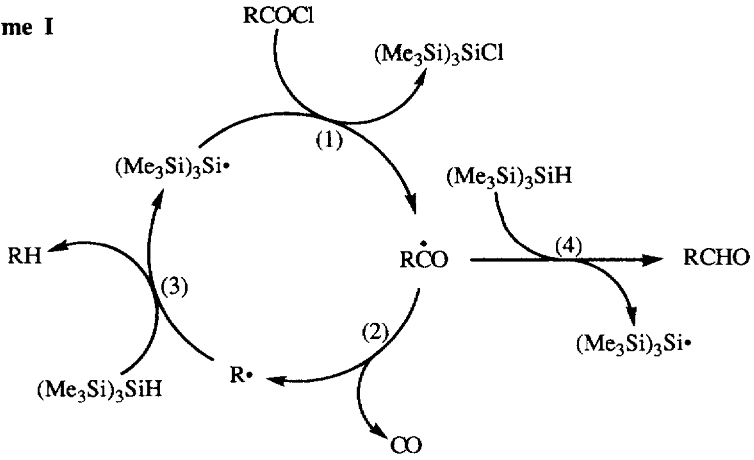
In view of the relevance of mechanistic knowledge to synthetic applications, we designed a series of experiments to determine the actual mechanism involved. Table II shows product formation and their yields for the reduction of primary, secondary and tertiary acid chlorides under low conversions (ca. 30%) at 80°C.The decrease of aldehyde formation through the series primary, secondary and tertiary, indicates that a decarbonylation of acyl radicals takes place.[11] The mechanism that we conceive for the reduction of acid chlorides is outlined in Scheme I. That is, tris(trimethylsilyl)silyl radicals, initially generated by small amount of initiator, abstract a chlorine atom to form an acyl radical intermediate (eq. 1) which undergoes either an intermolecular hydrogen abstraction giving the aldehyde (eq. 4) or an α-scission to form an alkyl radical (eq. 2). Hydrogen abstraction from the silane by $R^\bullet$ regenerates the $(Me_3Si)_3Si^\bullet$ radicals (eq. 3), thus completing the cycle of this chain reaction.

Table II. Reaction of Acid Chlorides with Tris(trimethylsilyl)silane in Toluene at 80°C (initiated by AIBN)

RCOCl	t, min	Conv. %	RH Yield, %	RCHO Yield, %	$RC(O)OCH_2R$ Yield, %
$CH_3(CH_2)_8COCl$	30	27	63	37	[a]
c-$C_6H_{11}COCl$	40	30	99	<1	—
$(CH_3)_3CCOCl$	30	38	98	—	—

[a] Small amounts

Scheme I



In the case of decanoyl chloride the formation of the ester $RCH_2OC(O)R$ as a minor product is also observed. Evidence that the ester derives from the aldehyde has also been obtained. That is, hydrosilylation of decanal under the same reaction conditions gave the corresponding silyl ether[12] (eq. 5) which underwent a spontaneous reaction with acid chloride to form the expected ester (eq. 6).

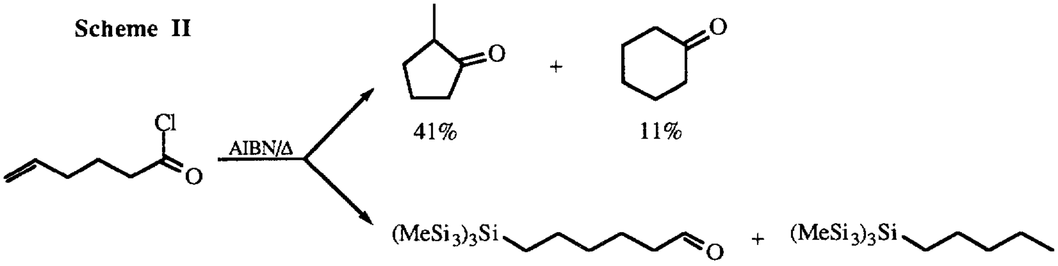
$$RCHO + (Me_3Si)_3SiH \xrightarrow{AIBN/\Delta} RCH_2OSi(SiMe_3)_3 \tag{5}$$

$$RCH_2OSi(SiMe_3)_3 + RCOCl \longrightarrow RCH_2OC(O)R + (Me_3Si)_3SiCl \tag{6}$$

In Scheme I, reactions 2 and 3 have been studied in some detail and activation parameters are available for a number of radicals.[11,13] In this work, we have performed some competitive studies in order to obtain kinetic information regarding reactions 1 and 4. That is, (i) the relative reactivity of *t*-BuCl and *t*-BuCOCl towards $(Me_3Si)_3Si^\bullet$ were obtained by GC analysis followed by the thermally initiated reaction between the silane and the two chlorides. A value of $k_{RCOCl}/k_{RCl} = 0.6$ at 80°C was calculated from the loss of starting materials by using the method of Ingold and Shaw.[14] Taking $k_{RCl} = 4.0 \times 10^5$ $M^{-1}s^{-1}$ at 25°C[15] and assuming $\log(A/M^{-1}s^{-1}) = 8.7$ we estimated k_1 to be ca. 7×10^5 $M^{-1}s^{-1}$ at 80°C. (ii) Using the decarbonylation of primary alkyl substituted acyl radicals as a timing device (free radical clock[16]) we obtained $k_2/k_4 = 0.41$ M at 100°C. Taking $k_2 = 4.0 \times 10^4$ s^{-1},[11] we calculated $k_4 = 1.0 \times 10^5$ $M^{-1}s^{-1}$ at 100°C.

The free radical cyclization of 5-hexenoyl chloride using Bu_3SnH as a mediator has also been performed.[3,17] However, the results are mechanistically irrelevant as free radical processes and spontaneous reactions occur together. This may explain the disagreement in the literature regarding the relative yields of 2-methylcyclopentanone and cyclohexanone. The reaction of 5-hexenoyl chloride (0.30 M) with $(Me_3Si)_3SiH$ (1.2 equiv) in toluene with catalytic amounts of AIBN (10%) at 80°C after 3 h was analysed by GC. The formation of 2-methylcyclopentanone (41%) and cyclohexanone (11%) were accompanied by two hydrosilylating products in ca. 1:2 ratio (see Scheme II) whose structures have been assigned on the basis of GC/MS spectra. These results, although preliminary, indicate that (i) the olefinic and acid chloride moieties have comparable reactivities towards the $(Me_3Si)_3Si^\bullet$ radical, in accordance with the present and previous studies[18] and (ii) the acyl radical cyclizes to give mainly a 5-membered ring with a rate constant at least 50 times faster than the decarbonylation process ($k_2 = 1.3 \times 10^4$ s^{-1} at 80°C).[11]

Scheme II



In conclusion, tris(trimethylsilyl)silane, contrary to tributyltin hydride, functions as a free radical reducing agent for aliphatic acid chlorides. This procedure could be an alternative to the Barton reaction for the free radical decarboxylation of carboxylic acids via the acyl derivatives of N-hydroxy-2-thiopyridone.[6] Further work on the kinetics and synthetic scope of these reactions is in progress.

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References and Notes

1. For reviews, see: Kupchik, E. J. In *Organotin Compounds*; Sawyer, A. K., Ed.; Marcel Dekker: New York, 1971; vol 1, pp 28-33. Kuivila, H. G. *Synthesis* **1970**, 499.
2. Neumann, W. P. *Synthesis* **1987**, 665 and references cited therein.
3. Lusztyk, J.; Lusztyk, E.; Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 2923. Lusztyk, J.; Lusztyk, E.; Maillard, B.; Lunazzi, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 4475.
4. Kuivila, H. G.; Walsh, E. J., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 571. Walsh, E. J., Jr.; Kuivila, H. G. *J. Am. Chem. Soc.* **1966**, *88*, 576.
5. Walsh, E. J., Jr.; Stoneberg, R. L.; Yorke, H.; Kuivila, H. G. *J. Org. Chem.* **1969**, *34*, 1156.
6. Barton, D. H. R. *Aldrichimica Acta* **1990**, *23*, 3 and references cited therein.
7. Billingham, N. C.; Jackson, R. A.; Malek, F. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1137.
8. Oka, K.; Nakao, R.; Abe, Y.; Dohmaru, T. *J. Organometal. Chem.* **1990**, *381*, 155.
9. Chatgilialoglu, C. *Acc. Chem. Res.*, in press.
10. Samples analyses were carried out by using GC and GC/MS using autentic samples as calibrants. Conversions and yields were quantified by GC using decane as an internal standard.
11. Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200. Vollenweider, J.-K.; Paul, H. *Int. J. Chem. Kinet.* **1986**, *18*, 791.
12. Alberti, A.; Chatgilialoglu, C. *Tetrahedron* **1990**, 46, 3963. Kulicke, K. J.; Giese, B. *Synlett* **1990**, 91.
13. Chatgilialoglu, C.; Dickhaut, J.; Giese, B. *J. Org. Chem.* **1991**, *56*, 6399.
14. Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918.
15. Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1989**, *54*, 2492.
16. Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.
17. Cekovic, Z. *Tetrahedron Lett.* **1972**, 749. Walsh, E. J., Jr.; Messinger, J. M., II; Grudoski, D. A.; Allchin, C. A. *Tetrahedron Lett.* **1980**, *21*, 749. Cekovic, Z.; Cvetkovic, M.; Dokic, G. *Glas. Hem. Drus. Beograd* **1981**, *46*, 238.
18. Ballestri, M.; Chatgilialoglu, C.; Clark, K. B.; Griller, D.; Giese, B.; Kopping, B. *J. Org. Chem.* **1991**, *56*, 678.

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