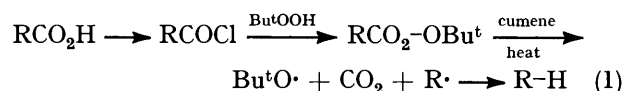


Free Radical Reactions in Solution. Part 4.¹ Radical-initiated Reduction of Acid Chlorides to Alkanes by Tri-*n*-propylsilane: Removal of Unwanted Carboxy-groups from Organic Molecules

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Aliphatic acyl chlorides RCOCl react with tripropylsilane in the presence of *t*-butyl peroxide at 140–170° to give the corresponding alkane RH. Yields are good when R is a primary or secondary alkyl group, poor when R is tertiary or benzylic, and zero when R is phenyl. A radical chain reaction is postulated. The reaction should be synthetically useful for removing carboxy-groups from carboxylic acids RCO₂H, where R is a primary or secondary alkyl group.

DECARBOXYLATION of non-activated alkanecarboxylic acids is not easy.² Recent syntheses which have involved the need for such decarboxylations include the synthesis of strained ring molecules³ and seco-steroids⁴ for which the reactions (1) have been employed. Yields



have only been fair (30–45%, or up to 55% if ethyl phenylacetate⁵ is used as the hydrogen donor rather

RESULTS AND DISCUSSION

We obtained reasonable yields of alkanes RH from a number of acid chlorides RCOCl by heating the acid chloride with tripropylsilane (*ca.* 2 mol equiv.) and *t*-butyl peroxide (*ca.* 1 mol equiv.) in an alkane solvent for 2–4 h at 140–170°. The reactions were normally carried out in degassed ampoules. As the Table shows, yields were good where R is a primary or secondary alkyl group, poor when R is tertiary or benzylic, and only traces of benzene were obtained where R is phenyl.

The main features of the reaction can be explained in

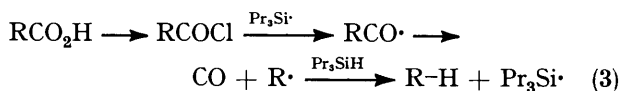
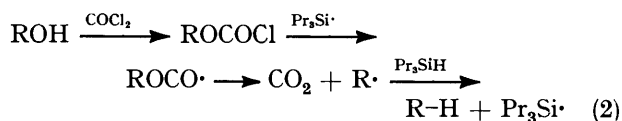
Reaction of acid chlorides RCOCl with Pr₃SiH and (Bu^tO)₂

R	Reagents (mole per mole of RCOCl)			T/°C	t/h	Yield (%) of RH ^a
	Pr ₃ SiH	(Bu ^t O) ₂	Dodecane			
n-Pentyl	1.9	0.9	10.7	160	4	56
C ₆ H ₅ CH ₂ CH ₂	2.1	0.8	13.1	140	2	55
Cyclohexyl	2.0	1.0	9.3	170	0.8	68
Cyclohexyl	2.0	1.0		140	4	48 ^b
1-Adamantyl	2.6	1.3		140	16 ^c	13 ^b
Benzyl	1.8	0.6		140	4	6
Phenyl	2	0.5	12.9	140	4	Trace

^a By g.l.c. unless indicated. ^b Isolated. ^c Substantially similar yields after 4 h.

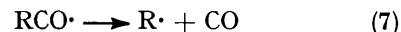
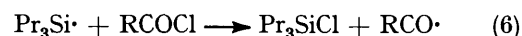
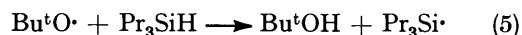
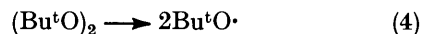
than cumene). A number of bridgehead carboxylic acids have recently been decarboxylated in good yield by a two-stage process involving conversion of the carboxylic acid to the bromide by a modified Hunsdiecker reaction, followed by reduction of the bromide by tri-*n*-butyltin hydride.⁶

Our recent successful dehydroxylation of alcohols *via* the chloroformate by a reaction involving tripropylsilyl radicals⁷ [reaction (2)] suggested that decarboxylation of carboxylic acids might be feasible by an analogous route *via* the acid chloride [reaction (3)]. This paper



describes our investigation of such a decarboxylation sequence.

terms of reactions (4)–(8). *t*-Butoxyl radicals are known to abstract hydrogen atoms from organosilanes even at low temperatures,⁸ and organosilyl radicals



efficiently abstract halogen atoms from a wide variety of organic halides (*e.g.* ref. 9). Fragmentation of RCO· to R· + CO is important in aldehyde degradation reactions: at the temperatures employed in our reactions we would expect reactions of type (7) to be fast for all the compounds we studied except perhaps where R = Ph (see below). Likewise the hydrogen abstraction step (8) is expected to be fast, at least for primary and secondary alkyl radicals.

Choice of Silane.—Organosilicon hydrides and organotin hydrides should both carry out halogen abstraction

reactions of type (6) efficiently, and organotin hydrides would be expected to react with alkyl radicals by

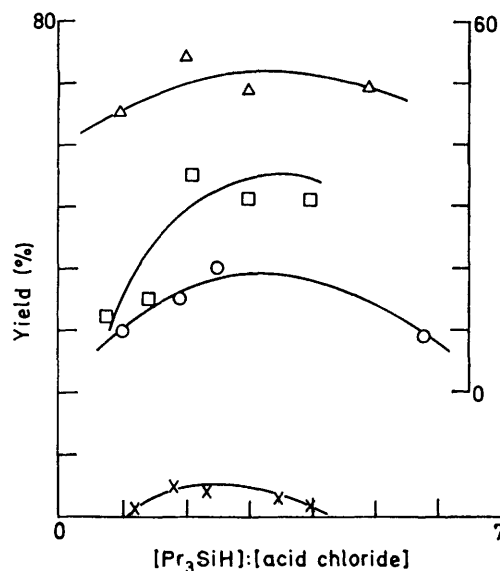


FIGURE 1 Reduction of acid chlorides with tripropylsilane. Variation of hydrocarbon yields with tripropylsilane concentration: \circ , pentane, moles *t*-butyl peroxide 0.9, moles dodecane solvent 11–14, 160°; \square , ethylbenzene, 0.8, 13, 140°; \triangle , cyclohexane (right-hand scale of percentage), 0.1, 14–15, 154°; \times , toluene, 0.6, 16, 170°

reactions of type (8) more efficiently than would organosilicon radicals. Nevertheless, we chose to work



with organosilicon hydrides because, for organotin hydrides, reactions of type (9; $\text{M} = \text{Sn}$) are fast enough

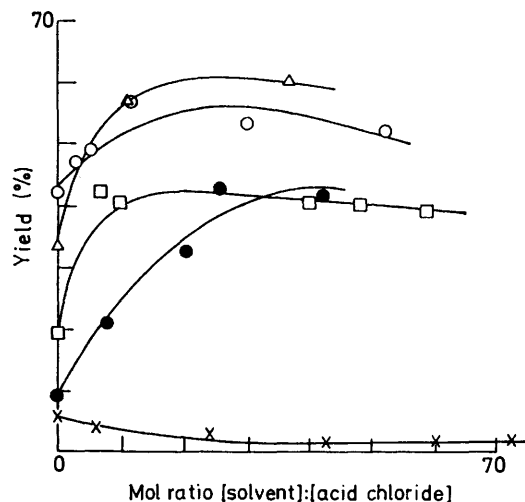


FIGURE 2 Reduction of acid chlorides with tripropylsilane. Variation of hydrocarbon yields with solvent (dodecane) concentration: \bullet , pentane, 140°, moles tripropylsilane 1.9, moles *t*-butyl peroxide 1.0; \circ , pentane, 160°, 1.9, 1.0; \square , ethylbenzene, 140°, 2.3, 0.8; \triangle , cyclohexane, 140°, 1.8–2.0, 1.0–1.1; \times , toluene, 140°, 1.8, 0.6

to compete effectively with the fragmentation reaction (7), and thus yields of the hydrocarbon are lowered.¹⁰

Tripropylsilane was chosen for the present work because of its convenient b.p. in relation to the reaction temperatures employed (110–170°) and the volatility of the hydrocarbon products. Other trialkylsilanes would be expected to give similar results, but as indicated later, methyl hydrogen polysiloxane gave poorer yields.

Figure 1 shows that the optimum amount of tripropylsilane is *ca.* 2 moles per mole of acid chloride. The slow fall off in yield at higher concentrations of tripropylsilane is an indication that reactions of type (9; $\text{M} = \text{Si}$) do not compete too seriously with reaction (7) in this system.

We carried out some experiments using methyl hydrogen polysiloxane (MeHSiO)_{*n*}, Dow Fluid 1107, since its commercial availability and low volatility would make it attractive as a reagent. Unfortunately, yields

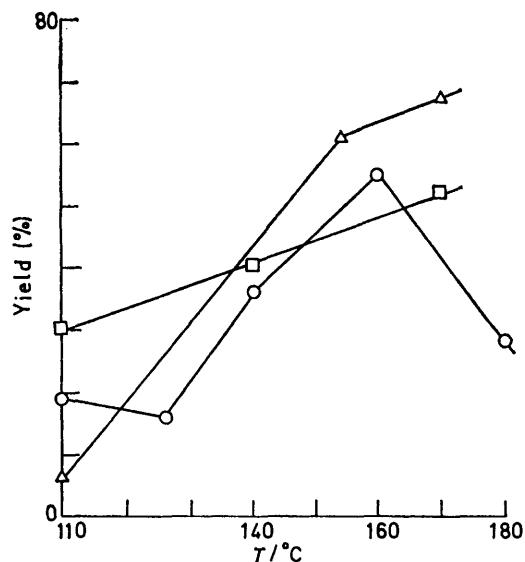


FIGURE 3 Reduction of acid chlorides with tripropylsilane. Variation of hydrocarbon yields with temperature: \circ , pentane, moles tripropylsilane 1.9, moles *t*-butyl peroxide 1.0–1.1, moles dodecane 11–19; \square , ethylbenzene, 1.7–2.3, 0.8–0.9, 12–16; \triangle , cyclohexane, 2, 1.0–1.3, 9–13

were consistently poorer than when tripropylsilane was used. This could be due to the polymeric nature of the silane, or to the presence of Si–O bonds in the molecule: parallel experiments¹¹ on conversion of chloroformate esters to alkanes favour the second explanation.

Solvent.—Figure 2 shows the effect of the presence of an inert solvent (dodecane) on hydrocarbon yields. Except for phenylacetyl chloride, there is an increase in yield when up to 10–20 moles of solvent per mole of acid chloride is used, with no significant change (possibly a slight fall off) when solvent in excess of this amount is added. This accords with the reactions (4)–(8) since for a constant ratio of the reaction components, dilution will favour the first-order decarbonylation reaction (7), which leads to alkane, over the second-order hydrogen transfer reaction (9) which does not. For phenylacetyl chloride however, the yields are slightly better in the absence of solvent. Here the decarbonylation reaction

(7) will be expected to be very fast indeed: the low overall yield in this case is attributed to the difficulty of benzyl radicals abstracting a hydrogen atom from tripropylsilane [reaction (8)].

Initiator.—*t*-Butyl peroxide was used as the initiator in most experiments. Yields were better at higher temperatures (140–170°) rather than at low temperatures (110°) (Figure 3). Attempts to initiate reaction by u.v. illumination, which would have allowed the use of higher temperatures, were unsuccessful.

A completely unexpected feature of the reaction is the large amount of *t*-butyl peroxide needed. As Figure 4 shows, amounts of *ca.* 0.4–1.2 mole peroxide per mole of acid chloride gave the maximum yield of alkane. Smaller amounts of peroxide gave very much reduced yields, whereas larger amounts for the most part only reduced yields by a small percentage.

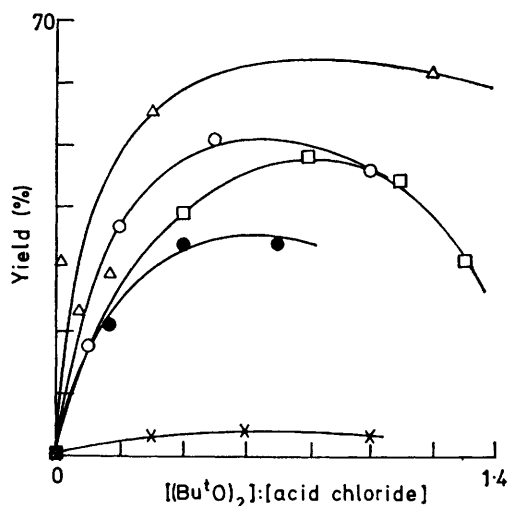


FIGURE 4 Reduction of acid chlorides with tripropylsilane (2 mol). Variation of hydrocarbon yields with *t*-butyl peroxide concentration: ●, pentane, 140°, moles dodecane 7; ○, pentane, 160°, 7; □, ethylbenzene, 140°, 18; △, cyclohexane, 154°, 12–14, ×, toluene, 140°, 13

We carried out a number of experiments to throw light on the need for the high concentration of peroxide. By measuring the residual *t*-butyl peroxide concentration in a number of experiments which had been carried out for different times at 140°, we were able to obtain a very rough rate constant of $1 \times 10^{-4} \text{ s}^{-1}$ for the first-order rate of disappearance of *t*-butyl peroxide in the presence of hydrocinnamoyl chloride. The points for the reaction in the presence of cyclohexanecarbonyl chloride were even more scattered, but indicated a rate of decomposition faster than in the presence of hydrocinnamoyl chloride (no appreciable amount of peroxide was left after 4 h). In the absence of an acid chloride, the rate of decomposition of *t*-butyl peroxide in tripropylsilane was *ca.* $6.5 \times 10^{-5} \text{ s}^{-1}$, so this rather limited evidence suggests that induced decomposition of the *t*-butyl peroxide by one of the intermediate radicals present in the system is taking place. Since the rate of decomposition of *t*-butyl peroxide in tripropylsilane

appears to be somewhat slower than in an inert solvent (k_{140° in cumene would be $9.2 \times 10^{-5} \text{ s}^{-1}$) in which induced decomposition is not thought to be important¹² it is unlikely that tripropylsilyl radicals are involved in the induced decomposition reaction, which makes the RCO· radical appear the most plausible contender. A relevant analogy may be the oxygen-containing radicals of type $\text{Ar}-\dot{\text{C}}\text{H}-\text{O}-\text{CH}_3$ which have been shown to cause induced decomposition of *t*-butyl peroxide in solution.¹³ The formation of *ca.* 9% of *t*-butyl phenylacetate from phenylacetyl chloride also provides support for the occurrence of induced decomposition.

Type of Acid Chloride Used.—The Table shows that reasonable yields of hydrocarbons are obtained when R is a primary or secondary alkyl radical. Poor yields are obtained when R is a tertiary or benzylic radical and only traces of product are obtained when R is phenyl. Thus there is no correlation of yield with reactivity of the intermediate radical.

We suggest that this variation can in fact be explained in terms of the effects of radical stability on the chain propagating reactions (6)–(8). Reaction (6), the removal of chlorine from the acid halide will be expected to proceed rapidly for all the acid halides. Hence no bottleneck will occur at this step. The decarbonylation reaction (7) will be expected to be fast for all the acyl radicals used, except for the benzoyl radical. Reactions of this type have been shown to be rapid even at 40° for $\text{R} = \text{Pr}^i, \text{Bu}^t$, and benzyl.^{14,15} Extrapolation of the data for reaction (7; $\text{R} = \text{Bu}^t$ and Pr^i) to give a value for k_7 ($\text{R} = \text{Et}$) or use of the Arrhenius parameters for reaction (7; $\text{R} = \text{Et}$) determined in the gas phase,¹⁶ both suggest that reaction (7) should be very fast for primary radicals at 170°. No kinetic data appears to be available for the fragmentation of $\text{PhCO}\cdot$ though the reaction is known to be slow¹⁷ at temperatures in the region of 70–80°. However, using the available gas phase data¹⁸ for $\text{CH}_3\text{CO}\cdot$ and assuming that the *A* factors for the two fragmentations are the same, and that the Polanyi relationship holds with $\alpha = \frac{1}{2}$, the half-life for (7; $\text{R} = \text{Ph}$) at 170° is calculated to be *ca.* 0.4 s. Thus in view of the fact that in radical chain reactions a half-life of *< ca.* 0.01 s is necessary for a radical in a particular step, it appears that the poor yield of benzene from benzoyl chloride may be due to the slowness of the fragmentation step (7).

The only pertinent kinetic data for the hydrogen transfer reaction (8) refer to the abstraction of hydrogen from trimethylsilane by methyl radicals.¹⁹ On the assumptions (1) that Pr_3SiH and Me_3SiH will react at the same rate, (2) that *A* factors are the same for all reactions of this type, (3) that reactions in solution proceed at the same rate as reactions in the gas phase, and (4) that the Polanyi relationship holds with $\alpha = \frac{1}{2}$, use of C–H bond dissociation energy data²⁰ gives $t_{\frac{1}{2}}$ for reactions of type (8) at 170° for phenyl, primary alkyl, secondary alkyl, *t*-alkyl, and benzyl radicals as *ca.* $1 \times 10^{-6}, 1 \times 10^{-3}, 7 \times 10^{-3}, 4 \times 10^{-2}$, and 2 s respectively. Thus reactions of type (8) should be fast

for phenyl and primary and secondary radicals at 170°, but t-alkyl and benzyl radicals should only react slowly with a consequential reduction in yield of hydrocarbon in these cases. Hence in this decarbonylation sequence it appears that yields from PhCOCl are low because of the slowness of step (7) whereas for t-alkyl and benzyl radicals, yields are poor because of the slowness of step (8). Only when R is primary or secondary do both pertinent steps in the chain reaction proceed rapidly, thus giving a good yield. A similar reactivity order is found for the related reaction, the conversion of chloroformate esters into hydrocarbons *via* the R-O-C=O radical where a similar explanation is likely.⁷ An analogous series of radical chain reactions where overall reactivity is highest in the middle of a series is the free radical addition of the hydrogen halides HF, HCl, HBr, and HI to ethylene.²¹

Thus when R is primary or secondary alkyl, our method appears to be a suitable procedure for the decarboxylation of carboxylic acids RCO₂H, and complements Langhals and R  chardt's method⁵ of decarboxylation of carboxylic acids where R is a tertiary alkyl group.

EXPERIMENTAL

Experiments involving organosilane reductions were carried out in degassed Pyrex ampoules and yields of hydrocarbon were determined by g.l.c. using an appropriate internal standard unless otherwise noted. Acid chlorides were either available commercially, or were made from the acid by the thionyl chloride method. Methyl hydrogen polysiloxane (Dow-Corning Fluid 1107) was used without further purification. Throughout, the use of the term mol indicates relative molar proportions rather than molar quantities unless a weight is given.

Decarbonylations.—The yields of alkane produced from the acid chlorides under a number of conditions are shown in the Table and Figures 1–4. Some further experimental results are given below to indicate in particular the range of experimental conditions used for particular compounds and attempts to initiate the reactions other than by t-butyl peroxide.

Benzoyl chloride. Variation of the amount of t-butyl peroxide (0–1 mol), tripropylsilane (0.9–4.8 mol), dodecane solvent (0–60 mol), and temperature (110–165°) gave in no instance more than a trace of benzene.

Photo-initiation (500 W medium pressure mercury lamp) of the reaction involving hydrocinnamoyl chloride at 216° gave a maximum yield of 4% ethylbenzene; phenylacetyl chloride at 150° gave only a trace of toluene.

Dibenzylmercury (0.2 mol) did not act as an efficient initiator for the reaction of hydrocinnamoyl chloride (1.0 mol) with tripropylsilane (2.2 mol) in the presence of dodecane (11.4 mol) at 140° for 5 h, when only a trace of ethylbenzene was obtained.

Experiments carried out under reflux (not in sealed ampoules). Cyclohexanecarbonyl chloride (1 mol), t-butyl peroxide (0.9 mol), tripropylsilane (1.6 mol), and dodecane (8.3 mol) when refluxed for 4 h gave only 5% of cyclohexane. Hydrocinnamoyl chloride (1 mol), t-butyl peroxide (0.8 mol), tripropylsilane (2.4 mol), and dodecane (9.7 mol) refluxed for 2 h gave only 9% of ethylbenzene.

Experiments using methyl hydrogen polysiloxane (MHPS).

All experiments were carried out at 140° for 4 h. (1) Hydrocinnamoyl chloride (1 mol), t-butyl peroxide (0.9 mol), dodecane (7–8 mol), and MHPS (2.4, 2.5, 4.7, 6.2, and 8.2 mol, expressed in terms of a single MeOSiH unit) gave ethylbenzene (12, 14, 26, 32, and 30%, respectively), compared with a range of 32–55% for analogous experiments with tripropylsilane. (2) Cyclohexanecarbonyl chloride (1 mol), t-butyl peroxide (0.9 mol), dodecane (7–8 mol), and MHPS (2.0, 2.8, 4.8, 6.0, and 6.3 mol) gave cyclohexane (20, 29, 42, 47, and 51%) compared with yields in the region of 60% for similar experiments using tripropylsilane. (3) Phenylacetyl chloride (1 mol), t-butyl peroxide (1 mol), dodecane (8.0 mol), and MHPS (2.6 mol) gave toluene (2%). (4) Benzoyl chloride (1 mol), t-butyl peroxide (1.0 mol), dodecane (8.0 mol), and MHPS (2.7 mol) gave no benzene.

Isolation experiments. (1) A mixture of adamantane-1-carbonyl chloride (332 mg, 1.65 mmol), tripropylsilane (679 mg, 4.3 mmol), and t-butyl peroxide (316 mg, 2.16 mmol) was degassed, sealed under vacuum in a Pyrex ampoule, and heated at 140° for 16 h. Excess of starting material was evaporated under high vacuum, and sublimation of the crude powdery product gave adamantane (30.3 mg, 13%), m.p. 202°, i.r. and n.m.r. identical with those of authentic material. In the absence of t-butyl peroxide, no adamantane was produced. (2) A mixture of cyclohexanecarbonyl chloride (1.008 g, 6.88 mmol), tripropylsilane (2.205 g, 13.9 mmol), and t-butyl peroxide (1.025 g, 7.01 mmol) was degassed and heated in an ampoule for 4 h at 140°. The reaction product was poured into water and the organic layer was dried (CaCl₂) and fractionated through a short column, yielding cyclohexane (0.28 g, 48%).

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