

Radical-initiated Reduction of Chloroformates to Alkanes by Tri-*n*-propylsilane. A Method for Removal of Unwanted Hydroxy-Groups from Organic Molecules^{1,2}

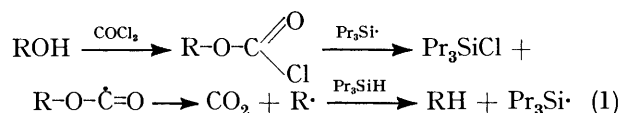
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Chloroformates of primary and secondary alcohols, produced by the reaction of the alcohol with phosgene, are reduced to the corresponding alkane in excellent yields by reaction with tri-*n*-propylsilane in the presence of *t*-butyl peroxide at 140 °C. Unusually large amounts of initiator are required [0.5–1.1 mol (Bu^tO)₂ per mol of RO·CO·Cl]. The results are rationalized in terms of a free-radical reaction scheme.

CONVENTIONAL methods of reduction of the C–OH group to C–H in organic compounds usually involve reagents such as metal hydrides which will also attack other reducible groups in the molecule. In reactions where there is the possibility of a carbonium ion intermediate, rearrangement of the carbon skeleton is likely. For these reasons there has been considerable recent interest^{3–9} in novel reduction methods which avoid these disadvantages.

RESULTS AND DISCUSSION

Scheme 1 offers a possible means of selective removal of hydroxy-groups from organic molecules, even in the presence of other functional groups. There are precedents for each of the projected steps in the radical-chain mechanism, and we hoped to find conditions favourable to the overall reaction.



We obtained excellent yields of alkanes RH from primary and secondary alcohols by heating the chloroformate ROCOCl with 2–4 mol of tripropylsilane and 0.5–1 mol of *t*-butyl peroxide in degassed ampoules at 140 °C, usually with dodecane as solvent (Table). On

Reactions of chloroformates RO·CO·Cl with Pr₃SiH at 140 °C

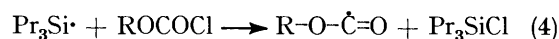
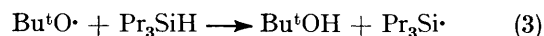
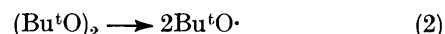
R	Reagents (mol per mol of RO·CO·Cl)			Time/h	% Yield of RH ^a
	Pr ₃ SiH	(Bu ^t O) ₂	C ₁₂ H ₂₆		
<i>n</i> -C ₈ H ₁₇	4.6	0.5	8	4	92
<i>n</i> -C ₉ H ₁₇	1.8	0.5	0	24	85 ^b
Cyclohexyl	3.2	0.9	13	4	91
C ₂₇ H ₄₇ ^d	3.4	1.1	49 ^e	24	69 ^{b,c}
Et ₃ C	1.8	1.0	17	4	18
PhCH ₂	1.9	0.9	0	8	11
Ph	1.9	0.6	12	4	Trace

^a Yields determined by g.l.c. unless indicated. ^b Isolated. ^c Yield based on original alcohol. ^d Cholestan-3β-yl. ^e Hexane used as solvent.

the other hand, yields of hydrocarbon from benzyl alcohol and 3-ethylpentan-3-ol were poor, and phenol gave only a trace of benzene.

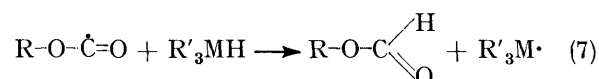
The main features of the reaction can be explained in terms of the free-radical scheme shown [equations (2)–

(6)]. *t*-Butoxy-radicals abstract hydrogen atoms from organosilanes even at low temperatures,¹⁰ and organosilyl radicals efficiently abstract halogen atoms from a wide variety of organic halides (*e.g.* ref. 11). We would



expect reaction (5) to be fast for all the compounds studied except possibly for phenyl chloroformate (see below). Likewise the hydrogen abstraction reaction (6) should be fast at least for primary and secondary aliphatic radicals.

Choice of Silane.—In spite of the known efficiency of organotin hydrides in reactions analogous to (3), (4), and (6), we chose to work with organosilicon hydrides rather than organotin hydrides because the latter are known to reduce chloroformates to formates.¹² This implies that for organotin hydrides, reaction (7; M = Sn) competes effectively with the fragmentation of the alkoxy-carbonyl



radical [reaction (5)], thereby lowering the yield of alkane. Since the silicon–hydrogen bond in organosilanes is stronger than the tin–hydrogen bond in organotin hydrides,^{11a,13} reactions of type (7; M = Si) should be slower and thus allow reaction (5) to compete favourably. The high yields of alkane produced from primary and secondary chloroformates confirm that this is so.

Tri-*n*-propylsilane was chosen for the present work because of its convenient boiling point. Other trialkylsilanes would be expected to give similar results, but as indicated below, methylhydrogenpolysiloxane gave poorer yields.

Figure 1 shows that the yield of alkane rises sharply with the amount of tripropylsilane up to about 2 mol Pr₃SiH per mol of chloroformate and then levels off. The high yields produced and the fact that yields do not fall in the presence of an excess of tripropylsilane is a good indication that reaction (7) does not compete

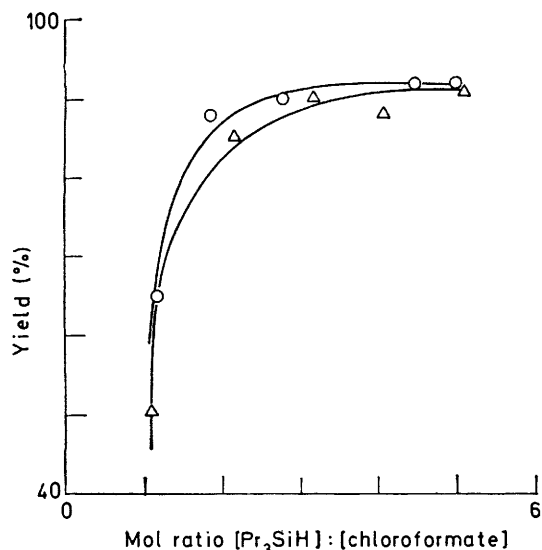


FIGURE 1 Reduction of chloroformates (1 mol) with tripropylsilane (4 h at 140 °C). Variation of hydrocarbon yield with tripropylsilane concentration. ○ octane, mol t-butyl peroxide 0.5, mol dodecane solvent 7.7; △ cyclohexane, 0.9, 13.1, respectively

significantly with reaction (5) when primary and secondary chloroformates are used.

We carried out some experiments using methylhydrogenpolysiloxane (OSiHMe_n), Dow Fluid 1107, since its commercial availability and low volatility make it attractive as a reagent. Unfortunately, yields were lower: the maximum yield of octane from n-octyl chloroformate was reduced from 92 to 61% when methylhydrogenpolysiloxane was used as the reducing agent,

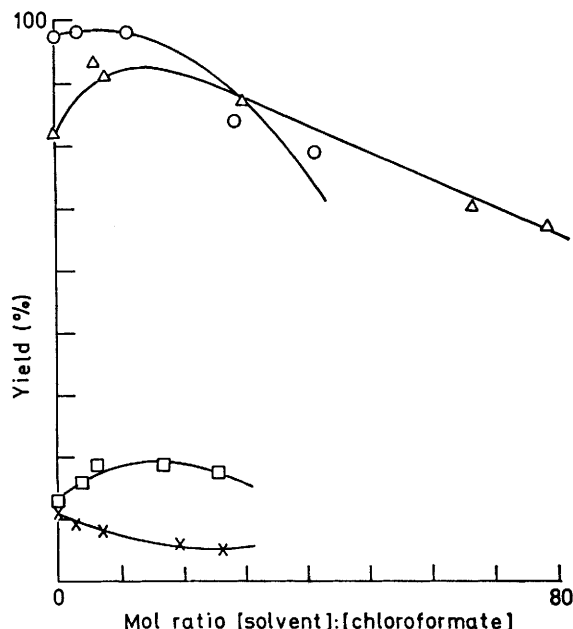


FIGURE 2 Reduction of chloroformates (1 mol) with tripropylsilane (4 h at 140 °C). Variation of hydrocarbon yield with solvent (dodecane) concentration. ○ octane, mol tripropylsilane 2.1, mol t-butyl peroxide 0.5; △ cyclohexane, 2.0, 0.9; □ 3-ethylpentane, 1.8, 1.0; × toluene, 1.9, 0.9 (8 h), respectively

though with cyclohexyl chloroformate the reduction in yield was less severe (91 to 84%). In experiments using triethoxysilane as the reducing agent, n-octyl chloroformate gave no octane. This indicates that it is the presence of Si-O bonds rather than the polymeric nature of the compound which makes methylhydrogenpolysiloxane less efficient than tripropylsilane as a reducing agent. This could be due to an unfavourable polar effect. In the transition state for the hydrogen-transfer reaction (6), the main polar contribution will be structure

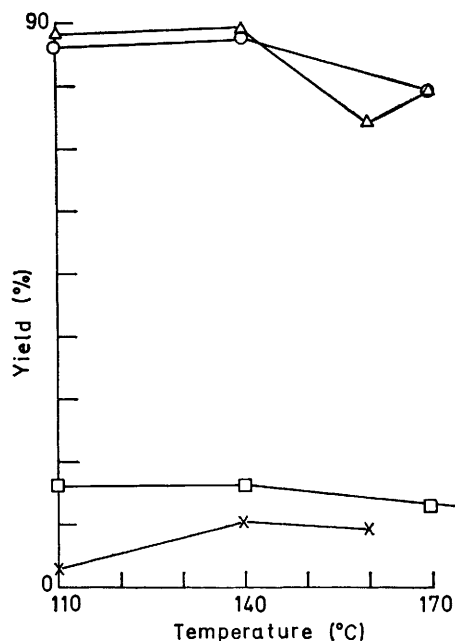
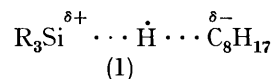


FIGURE 3 Reduction of chloroformates (1 mol) with tripropylsilane. Variation of hydrocarbon yield with temperature. Times: 72 h at 110 °C, 24 h at 140 °C, 3–4 h at 160 and 170 °C. ○ octane, mol tripropylsilane 1.8, mol t-butyl peroxide 0.5, mol dodecane solvent 6; △ cyclohexane, 2, 0.9, 11–14; □ 3-ethylpentane, 1.8, 0.9, 0; × toluene, 1.9, 0.9, 8, respectively

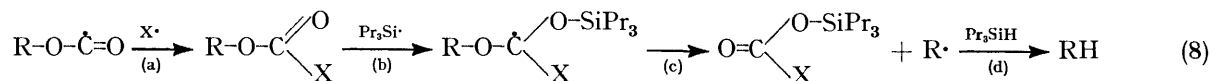
(1), and contributions from this polar form are expected to be less significant when $\text{R} = \text{OEt}$.



Solvent.—Figure 2 shows the effect of the use of dodecane as solvent on the yield. In contrast with the analogous reactions with acid chlorides where the presence of solvent is usually beneficial, there is a tendency for a large amount of solvent to decrease the yield and a small amount of solvent may or may not be beneficial, with an optimum amount of between 5–10 mol solvent per mol of chloroformate.

Initiator.—t-Butyl peroxide was used as the initiator in most of the experiments. Yields tended to be somewhat higher at 110 or 140 °C rather than 170 °C (see Figure 3) but the yield of toluene from benzyl chloroformate was lower at 110 °C. Attempts to photo-initiate the reaction at 150 °C in the absence of t-butyl peroxide were unsuccessful.

An apparently unprecedented feature of the reaction is the quantity of *t*-butyl peroxide required.* As Figure 4 shows, maximum yields of alkane are obtained at a peroxide : chloroformate ratio of 0.6 for octyl chloroformate and 1.0 for cyclohexyl chloroformate, with the yield of alkane dropping at higher peroxide concentrations. This appears *not* to be due to induced decomposition of the peroxide, since very rough kinetic experiments at 140 °C indicate a rate of decomposition of peroxide similar to that found in the absence of chloroformate. We suggest that the sequence of reactions (8)



may be responsible. If the radical chains are short, an appreciable proportion of the $\text{R-O}-\dot{\text{C}}=\text{O}$ radicals may be lost by combination reactions (8a; X = any other radical present in the system). This reaction sequence would

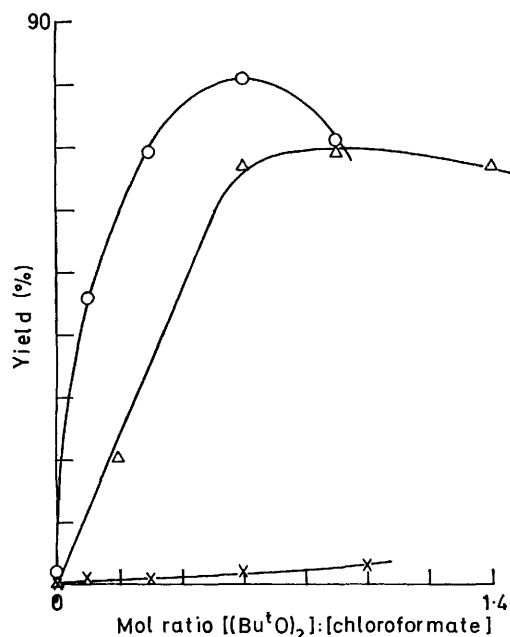


FIGURE 4 Reduction of chloroformates (1 mol) with tripropylsilane (2 mol) at 140 °C. Variation of hydrocarbon yield with *t*-butyl peroxide concentration. O octane, mol dodecane solvent 8, time 4 h; Δ cyclohexane, 13.5, 4; \times toluene, 10, 1, respectively

account for the high consumption of *t*-butyl peroxide and tripropylsilane (without increasing the rate of decomposition of the peroxide), whilst at the same time giving a good yield of the alkane product RH.

Type of Alcohol Used.—The Table shows that excellent yields of alkane are formed from primary and secondary alcohols, but that the method is less suitable for tertiary alcohols, benzylic alcohols, and phenols. Tertiary chloroformates are thermally unstable and give the corresponding alkene;¹⁴ this must in part be responsible for the

* We have also noted the need for a large amount of peroxide in the related reduction of acid chlorides to alkanes by tripropylsilane.¹

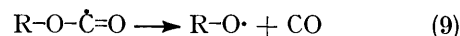
† The radical $\text{PhO}\dot{\text{C}}\text{O}$ does not lose CO_2 in solution at 75 °C.¹⁵

low yield of 3-ethylpentane formed from 1,1-diethylpropyl chloroformate. We tentatively ascribe the poor yields from phenyl and benzyl chloroformates to hold-ups in the propagation sequence (4)—(6). Reaction (6) should be fast at 170 °C for all the radicals studied except for tertiary and benzyl radicals, but for benzyl radicals reaction (6) may be slow enough to cut down the yield of alkane product.¹ This general pattern of reactivity will not be significantly different at 140 °C.

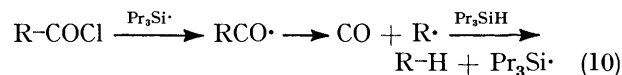
The low yield from phenyl chloroformate on the other hand may well be due to a slow step (5). The half-life

for $\text{PhO}\dot{\text{C}}\text{O}$ is estimated (see Experimental section for assumptions) to be *ca.* 0.1 s at 140 °C, for $\text{MeO}\dot{\text{C}}\text{O}$ a value of *ca.* 2×10^{-4} seconds is obtained, and all the other radicals studied should have shorter half-lives than this. On this basis, reaction (5) is a possible bottle-neck only for the $\text{PhO}\dot{\text{C}}\text{O}$ radical.†

It should also be noted that the phenoxycarbonyl radical, but not alkoxy carbonyl radicals, may fragment by the alternative route (9) which would not yield the hydrocarbon. The stabilization of the phenoxyl radical makes reaction (9; R = Ph) only *ca.* 2 kcal less unfavourable energetically than reaction (5), whereas when R = Me, the difference is *ca.* 36 kcal mol⁻¹. Louw and his co-workers¹⁶ found evidence that $\text{PhO}\dot{\text{C}}\text{O}$ does in fact fragment at 400—500 °C by reaction (9) rather than reaction (5).



Thus the poor yield from benzyl chloroformate is explained in terms of a slow step (6), and that from phenyl chloroformate by a probable slow step (5). Only for primary and secondary alkoxy carbonyl groups are steps (5) and (6) both fast, giving good yields. An analogous situation is found in the similar decarboxylation of acid chlorides¹ to alkanes by the sequence (10).

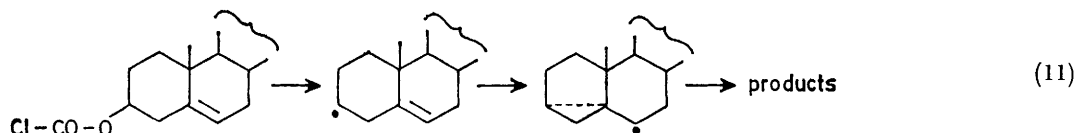


Compatibility with Other Functional Groups.—The yield of cholest-5-ene from cholesteryl chloroformate was only 25%. This may be due to attack by free radicals on the C=C double bond or at the allylic position, but the n.m.r. spectrum of the crude product indicated the possible presence of a cyclopropyl ring, which could have been formed by ring closure of the cholesteryl radical to give *i*-cholesteryl derivatives (reaction (11) (*cf.* ref. 17)). On the other hand the compound $\text{MeCO}[\text{CH}_2]_3\text{O}\cdot\text{CO}\cdot\text{Cl}$ gives pentan-2-one in yields of up to 69% showing that a hydroxy-group can be removed whilst leaving a ketone group unchanged.

Thus our procedure is of potential synthetic utility in removal of primary and secondary hydroxy-groups even in the presence of ketone groups. As noted above, the

method may be unsuitable for unsaturated alcohols. Functional groups which react with phosgene will interfere with the reaction. The compatibility of this method with the presence of other functional groups is being investigated further.

90–91 °C (Found: C, 87.45; H, 12.1. Calc. for $C_{27}H_{46}$: C, 87.5; H, 12.5%). The residual oil (0.81 g) was insoluble in boiling acetone, and attempts to crystallize it from a variety of solvents were unsuccessful. T.l.c. indicated the presence of two compounds with very similar R_F values.



EXPERIMENTAL

Experiments involving organosilane reductions were carried out in degassed Pyrex ampoules, and yields of hydrocarbon were determined by gas-liquid chromatography using an appropriate alkane as internal standard unless otherwise noted. Phenyl, benzyl, and cholesteryl chloroformates were commercially available. The other chloroformates were made by treating the corresponding alcohols with phosgene.¹⁸ Methylhydrogenpolysiloxane (Dow Corning Fluid 1107) was used without further purification. Throughout this paper, the use of 'mol' indicates relative molar proportions rather than molar quantities.

Dehydroxylation (via the Chloroformates).—The yields of alkanes 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 tried for particular compounds, and attempts to initiate the reactions other than by *t*-butyl peroxide.

***n*-Octyl chloroformate.** A solution of *n*-octyl chloroformate (3.69 g, 1 mol), tripropylsilane (5.48 g, 1.8 mol), and *t*-butyl peroxide (1.33 g, 0.5 mol) was heated at 140 °C for 24 h in a sealed ampoule. Distillation of the product gave octane (1.85 g, 85%), b.p. 125 °C, identified as authentic octane by i.r., refractive index, and retention times on three different g.l.c. columns. In addition to the sealed tube experiments, an experiment was carried out under reflux. *n*-Octyl chloroformate (1.0 mol), tripropylsilane (3.7 mol), *t*-butyl peroxide (0.4 mol), and dodecane (7.0 mol) with undecane as internal standard gave, after 24 h under reflux in the atmosphere, a yield for octane of 62%.

Cyclohexyl chloroformate. In addition to the sealed tube experiments (Figures 1–4), solutions of cyclohexyl chloroformate (1.0 mol), tripropylsilane (3.3 mol), *t*-butyl peroxide (0.9 mol), and dodecane (11.2 and 12.0 mol) with octane as internal standard gave, after 4 h reflux in the atmosphere, cyclohexane (42 and 45% respectively).

Cholestan-3 β -yl chloroformate. A mixture of cholestan-3 β -yl chloroformate (538 mg, 1 mol), tripropylsilane (649 mg, 3.4 mol), and *t*-butyl peroxide (184 mg, 1.1 mol) in hexane (5 g) was heated at 140 °C for 24 h. After evaporation of volatile components under vacuum, the residue was chromatographed on alumina (Grade I; acidic) with light petroleum (b.p. 60–80 °C). Crystallization from acetone-methanol gave cholestan-3 β -ene (341 mg, 77%), m.p. and mixed m.p. 78.5–79 °C, identified by t.l.c. and its i.r. and mass spectra.

Cholesteryl chloroformate. A mixture of cholesteryl chloroformate (1.4 g, 1 mol), tripropylsilane (1.3 g, 2.6 mol), and *t*-butyl peroxide (0.44 g, 1.0 mol) was treated as above and after chromatography gave an oil from which cholest-5-ene (0.29 g, 25%) was crystallized from acetone, m.p.

The i.r. spectrum showed no bands corresponding to the original chloroformate. The n.m.r. spectrum showed a sharp peak at τ 9.8 possibly due to the presence of a cyclopropane ring,^{17b} and a multiplet centred at τ ca. 8.9.

Phenyl chloroformate. Experiments carried out with phenyl chloroformate (1 mol), tripropylsilane (2 mol), and *t*-butyl peroxide (0.3–1.3 mol) in dodecane solvent (12 mol) with octane as internal standard at temperatures ranging from 110–180 °C gave in no instance more than a trace of benzene.

4-Oxopentyl chloroformate. Solutions of 4-oxopentyl chloroformate (1 mol), tripropylsilane (1.9–2.1 mol), and *t*-butyl peroxide (0.9–1.1 mol) with nonane as internal standard were heated at 140 °C for 4, 4, 8, 17, and 24 h. Yields of pentan-2-one were 49, 43, 51, 69, and 57%, respectively.

1,1-Diethylpropyl chloroformate. This compound decomposed when heated on its own at 140 °C. Solutions containing 1,1-diethylpropyl chloroformate (1.0 mol), tripropylsilane (1.8–1.9 mol), *t*-butyl peroxide (1.0 mol), and dodecane (0–26.2 mol) with octane as internal standard were heated at 140 °C for 4 h. Yields of 3-ethylpentane were in the range 13–18%. Variation of the reaction temperature from 110–170 °C had no appreciable effect on the yield of 3-ethylpentane.

Attempted photo-initiation. Attempts to photo-initiate the reactions involving cyclohexyl, benzyl, and phenyl chloroformates by light from a medium pressure mercury lamp in the absence of *t*-butyl peroxide at 150 °C gave zero-trace quantities of the desired hydrocarbons.

Rate of Disappearance of *t*-Butyl Peroxide.—Stock solutions of various chloroformates, *t*-butyl peroxide, and tripropylsilane in an alkane solvent with a suitable internal standard were divided between six ampoules which were heated at 140 °C for times between 0 and 24 h. From the *t*-butyl peroxide remaining after different times, the following approximate rate constants were determined: *n*-butyl chloroformate, $5 \times 10^{-5} \text{ s}^{-1}$; *n*-octyl chloroformate, $8 \times 10^{-5} \text{ s}^{-1}$; cyclohexyl chloroformate, $4 \times 10^{-5} \text{ s}^{-1}$; *n*-butyl chloroformate in the absence of tripropylsilane, $7.5 \times 10^{-5} \text{ s}^{-1}$; no chloroformate present, $6.5 \times 10^{-5} \text{ s}^{-1}$ (calculated rate constant for decomposition of *t*-butyl peroxide in cumene from the data of ref. 19: $9.2 \times 10^{-5} \text{ s}^{-1}$).

Experiments using Methylhydrogenpolysiloxane (OSiMeH)_n (MHPS).—(Molar equivalents of this compound are expressed in terms of a single OSiMeH unit.) All experiments were carried out at 140 °C for 4 h. (1) *n*-Octyl chloroformate (1 mol), MHPS (4.1–7.7 mol), *t*-butyl peroxide (0.5 mol), and dodecane (6.7–7.5 mol) with undecane as internal standard gave yields of octane in the range 51–61%. (2) Cyclohexyl chloroformate (1 mol), MHPS (1.5, 3.4, 6.8, and 12.4 mol), *t*-butyl peroxide (1.0 mol), and

dodecane (10.6—12.3 mol) with octane as the internal standard gave cyclohexane (42, 58, 84, 61% respectively).

Experiments using Triethoxysilane.—Solutions of n-octyl chloroformate (1.0 mol), triethoxysilane (1.9—6.4 mol), t-butyl peroxide (0.5 mol), and dodecane (8.2—8.4 mol) with undecane as internal solvent were heated at 140 °C for 4 h. No octane was detected.

Thermochemical Estimates. ΔH Values for reactions (5) and (9) were calculated to be -0.4 and $+1.6$ kcal mol⁻¹ (R = Ph) and -11 and $+25$ kcal mol⁻¹ (R = Me), respectively, by using the data of ref. 20. In estimating rate constants for reactions of type (5) it was assumed that all Arrhenius A factors were $10^{13.4}$ s⁻¹ (as is the case²¹ when R = Bu^t), that ΔH for reactions (5) with different alkyl radicals would reflect the different stabilities of the alkyl radicals produced [as measured by differences in $D(R-H)^{20b}$] and that the activation energies would change from those reported²¹ for reaction (5; R = Bu^t) by half these differences [using the Polanyi relationship with $\alpha = 0.5$], giving $E_5 = 18.5$ (R = Me) and 23.9 kcal mol⁻¹ (R = Ph). The fragmentation of n-C₃H₇OCO· has been studied in the gas phase by Cadman, White, and Trotman-Dickenson²² who deduced $E_5 = 12.7$ kcal mol⁻¹ for this system, and from this data, Louw and his co-workers¹⁶ estimate $E_5 = 23$ kcal mol⁻¹ (R = Ph), which supports the idea that reaction (5) may be slow at 140 °C when R = Ph but will be fast for all the other radicals considered.

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