

Polar Effects in Free-Radical Reactions. The Paradox of Reduction of Alkyl Iodides and Reductive Alkylation of Alkenes by Strong Oxidants (*t*-BuOOH, Pb(OAc)₄)

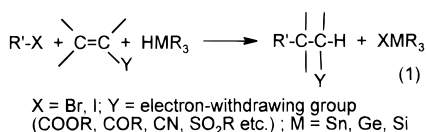
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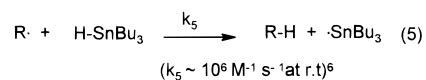
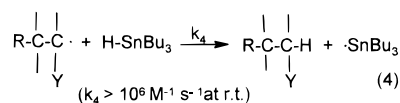
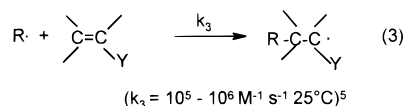
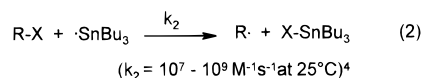
Received February 9, 1999. Revised Manuscript Received June 25, 1999

Abstract: Alkanes are directly iodinated by perfluoroalkyl iodides by a free-radical chain process initiated by *t*-BuOOH in acetic acid solution. The initially formed iodoalkanes are reduced back to alkanes by excess *t*-BuOOH; the rate constant for hydrogen abstraction from *t*-BuOOH by a primary alkyl radical has been roughly evaluated to be $\sim 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Two new procedures for the reductive alkylation of alkenes by *t*-BuOOH and Pb(OAc)₄ are reported. The importance of the polar effects and the rate constants of the key elementary steps involved in these processes is discussed.

The reductive alkylation of electron-poor alkenes by nucleophilic alkyl radicals generated from alkyl halides and metal hydrides (Bu₃SnH,¹ Bu₃GeH,²) or by some silanes, such as (Me₃-Si)₃SiH,³ has been developed during the last fifteen years as one of the major methodologies of the organic synthesis for the formation of carbon–carbon bonds (eq 1). The kinetic



rationale for the synthetic success is related to the absolute rate constants (k_2 – k_5) of the elementary steps involved in the radical chain processes, which in the case of the most utilized hydride, Bu₃SnH, are described by eqs 2–5.



Only with the most reactive alkenes, CH₂=CH–Y (Y = CN, CHO, COOR, COR etc.) is k_3 of the same order of magnitude

(10^5 – $10^6 \text{ M}^{-1} \text{ s}^{-1}$)⁵ as k_5 ($\approx 10^6 \text{ M}^{-1} \text{ s}^{-1}$)⁶ at room temperature with simple unsubstituted alkyl radicals, R \cdot . Thus, even with the most reactive alkenes, the steady-state concentration of Bu₃SnH must be kept low compared to the alkene concentration, to minimize reaction 5 and make the reductive alkylation successful.

The reductive alkylation, according to eq 1, has much less synthetic interest with simple unconjugated alkenes, because hydrogen abstraction from Bu₃SnH by alkyl radicals is too much faster⁶ ($10^6 \text{ M}^{-1} \text{ s}^{-1}$) than alkyl radical addition to alkenes ($\approx 10^2 \text{ M}^{-1} \text{ s}^{-1}$).⁵ On the other hand, the reductive alkylation (eq 1) of electron-rich and electron-poor alkenes by electrophilic carbon-centered radicals, such as perfluoroalkyl radicals or alkyl radicals bearing electron-withdrawing groups (CN, COOR, COR, NO₂, etc.) in the α position, also shows poor synthetic interest. This is due to the fact that, in both cases, hydrogen abstraction from Bu₃SnH remains much faster^{6,7} than the addition of the electrophilic radical to the alkene, even if a considerable increase of reactivity is observed with electron-rich alkenes.⁵

In this paper, we report new synthetic developments which, starting from the paradoxical reduction of alkyl iodides by *t*-BuOOH, have led to the reductive alkylation of simple alkenes by electrophilic carbon-centered radicals. Moreover, we report a new methodology for the reductive alkylation of electron-

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poor alkenes by nucleophilic radicals generated by Pb(IV) oxidation of carboxylic acids. These new synthetic achievements were made possible by evaluation of the involved polar effects and by knowing the absolute rate constants of some key elementary steps of the reactions.

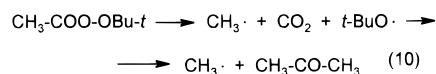
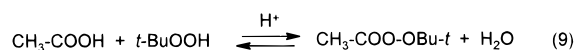
Results and Discussion

Homolytic Iodination of Alkanes by Perfluoroalkyl Iodides and Reduction of Alkyl Iodides by *t*-BuOOH. In a preliminary communication, we⁸ have reported a new direct homolytic iodination of alkanes by perfluoroalkyl iodides, R_fI, in a chain process (eqs 6 and 7) initiated by *t*-BuOOH in acetic acid. The interest of this new method is related to the fact that the direct free-radical iodination of alkanes by iodine, unlike the other halogens, is not feasible owing to the large unfavorable enthalpy for hydrogen abstraction (eq 8).



$$\Delta H \sim 20\text{--}33 \text{ kcal/mol}$$

The initiation of the radical chain of eqs 6–7 occurs through the equilibrium of eq 9, favored by acid catalysis. The equilibrium is continuously shifted at right by the irreversible thermolysis of the perester (eq 10), which acts as effective source of methyl radical (β -scission is the main behavior of *tert*-butoxyl radical in refluxing acetic acid).⁹ *t*-BuOOH is not an efficient thermal initiator for free-radical chain processes, but it becomes efficient in AcOH solution through eqs 9 and 10: the rate constants for the unimolecular decomposition of CH₃-COO*t*-Bu and *t*-BuOOH are respectively 2×10^{-5} (120 °C) and 1×10^{-5} s⁻¹ (150 °C). Methyl radical initiates the chain process by abstracting iodine atom from perfluoroalkyl iodide (eq 11).



Iodine abstraction according to eqs 7 and 11 is very effective for both polar and enthalpic reasons (the R–I bond is expected to be stronger than the R_f–I bond). On the other hand, hydrogen abstractions from C–H bonds by R_f• radicals (eq 6) are >10³ times faster¹¹ than by the corresponding alkyl radicals R•, always for both polar and enthalpic effects (the R_f–H bond is stronger than the R–H bond). This makes the chain propagation (eqs 6 and 7) particularly effective. Actually, calculations¹² would indicate that the BDE of an R_f–H bond is not significantly different from that of an R–H bond, while experimental values indicate that the CF₃–H bond (BDE = 106.7 kcal mol⁻¹) is

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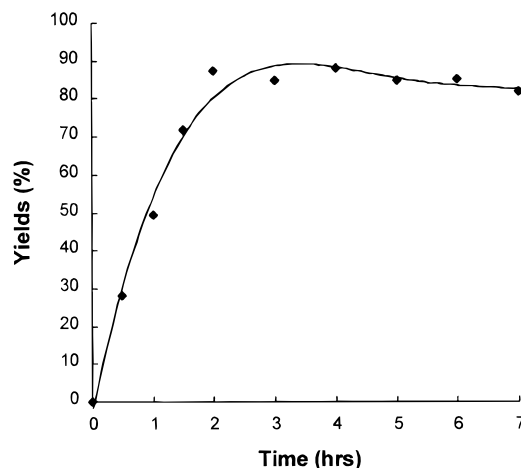


Figure 1. Iodination of cyclohexane (5 mL of cyclohexane, 5 mL of AcOH, 1 mmol of C₄F₉-I, and 2 mmol of *t*-BuOOH at 80 °C). Yields based on C₄F₉-I.

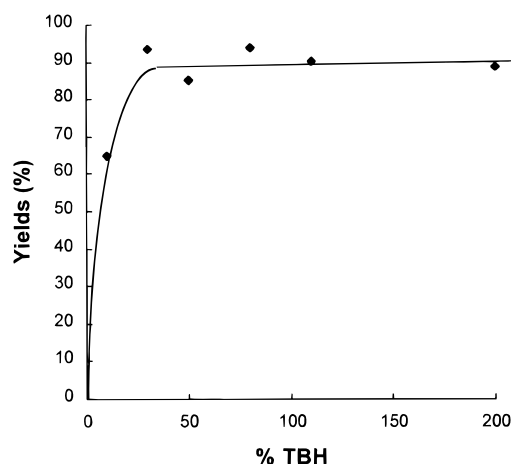


Figure 2. Iodination of cyclohexane (5 mL of cyclohexane, 5 mL of AcOH, 1 mmol of C₄F₉-I, and variable amounts of *t*-BuOOH at 80 °C). Yields and percentage of *t*-BuOOH based on C₄F₉-I.

stronger than CH₃-H (BDE = 104.8 kcal mol⁻¹)¹³ and the CF₃-CF₂-H bond (BDE = 102.7 kcal mol⁻¹) is stronger than CH₃-CH₂-H (BDE = 101.1 kcal mol⁻¹).¹⁴ However, we observed that the yields of alkane iodination in acetic acid were directly related to the amount of *t*-BuOOH. The yields of cyclohexane iodination related to the concentration of cyclohexane and *t*-BuOOH, to reaction time, and to temperature are reported in Figures 1–3; initially the yields rapidly increase at higher temperature (~100 °C) (Figure 3), but after a maximum value they slowly decrease. Our previous results,^{15,16} concerning the generation of alkyl radicals from alkyl iodides and methyl radical, suggested that this behavior should be due to the further reaction of alkyl iodides with the methyl radical. Actually, the results obtained with 1-iodododecane and iodocyclohexane indicate that alkyl iodides react with *t*-BuOOH under the same conditions, leading, paradoxically, mainly to the corresponding alkanes and for a minor extent to the alkenes. The equilibrium constants for iodine abstraction from primary, secondary, and

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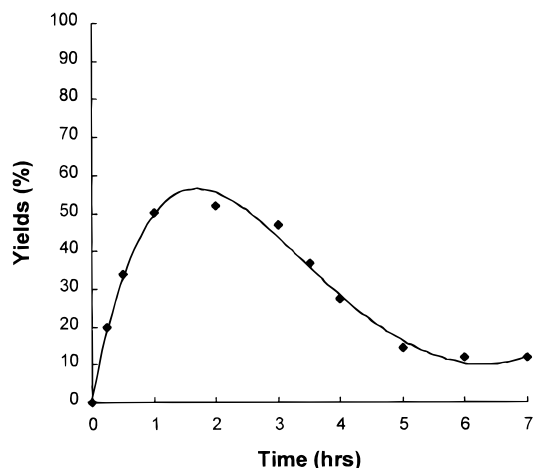
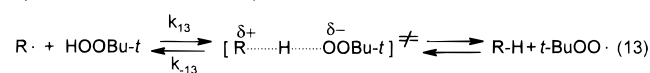
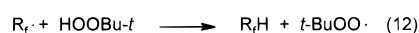


Figure 3. Iodination of cyclohexane (1 mL of cyclohexane, 9 mL of AcOH, 1 mmol of C_4F_9-I , and 2 mmol of t -BuOOH at 100 °C). Yields based on C_4F_9-I .

Table 1. Reaction of n - $C_{12}H_{25}-I$ with t -BuOOH

t -BuOOH (mmol)	dodecane (%)	1-dodecene (%)
0.1	78.6	21.4
0.3	87.0	13.0
0.5	87.8	12.2
0.8	89.6	10.4
1.1	91.1	9.9
2.0	100	0

tertiary alkyl iodides by methyl radical have been evaluated¹⁷ and correlated to the strengths of C–I bonds (56.5 kcal mol⁻¹ for CH_3-I and 52.1 kcal mol⁻¹ for t -Bu–I).¹⁷ The temperature effect is due to the thermolysis of the perester: at lower temperature (~80 °C) eq 10 is just fast enough for the initiation (traces of methyl radical are necessary) of an effective radical chain based on eqs 6 and 7, but not for a further significant reaction of the formed alkyl iodide, which requires a stoichiometric amount of methyl radical. To have high, almost quantitative yields of iodination, based on R_I , an excess of alkane is necessary; this is related, in our interpretation, to competition by eq 12, faster than eq 6, as will be discussed later on for the reactions of alkyl radicals. The formation of the alkane from the alkyl radical could be due to hydrogen abstraction from the solvent. However, we have investigated the ratio between alkane and alkene by changing the ratio between alkyl iodide and t -BuOOH and have observed that these ratios increase with the increasing amount of t -BuOOH, so that with an excess of this reagent only the alkane is formed (Table 1). This can be viewed as a specific paradox within the general paradox of a reductive process determined by a strong oxidant. This behavior has suggested to us that the reduction of the alkyl radical could be due more to hydrogen abstraction from t -BuOOH (eq 13) than from the solvent. The formation of only minor amounts of 1-dodecanol would indicate that hydrogen abstraction (eq 13) prevails over hydroxyl group transfer.



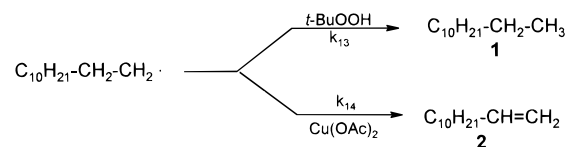
Reaction 13 is exothermic by ca. 10 kcal mol⁻¹ (bond energies are respectively ca. 89 and 99 kcal mol⁻¹ for $ROO-H$

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Table 2. Reaction of n - $C_{12}H_{25}-I$ with t -BuOOH and $Cu(OAc)_2$

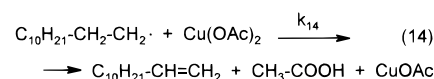
t -BuOOH (mmol)	$Cu(OAc)_2$ (mmol)	dodecane (%)	1-dodecene (%)
0.5	0.01	35.1	64.9
1	0.01	44.4	55.6
2	0.01	50.0	50.0
3	0.01	56.7	43.3
0.5	0.03	18.0	82.0
1	0.03	23.1	76.9
2	0.03	30.5	69.5
1	0.1	12.0	88.0

Scheme 1



$$\frac{k_{13}}{k_{14}} = \frac{[1] [Cu(OAc)_2]}{[2] [t-BuOOH]}$$

and RCH_2-H), so that the equilibrium of eq 13 is shifted at right. This equilibrium is of great general interest because it represents a key step of the autoxidation process and it would be particularly interesting to evaluate the absolute rate constants k_{13} , since a large number of k_{-13} values have been determined.¹⁸ In the autoxidation processes, the very fast (mostly diffusion-controlled) and irreversible reaction of alkyl radicals with oxygen shifts to the left the unfavorable reversed equilibrium of eq 13. We have investigated the same reaction with 1-iodododecane in the presence of variable amounts of t -BuOOH and of $Cu(OAc)_2$, which is well-known¹⁹ to oxidize alkyl radicals to alkenes (eq 14). Both dodecane and 1-dodecene were



formed; their ratio strictly depends on the ratio between $Cu(OAc)_2$ and t -BuOOH (Table 2) and this again suggests the involvement of eq 13 in the reduction.

Since the value of k_{14} is known ($2.7-3.1 \times 10^6 M^{-1} s^{-1}$ for n -Bu^{*} radical at 25 °C),¹⁹ it is possible, from Scheme 1 and the quantitative analysis of dodecane, 1-dodecene, and peroxide during the course of the reaction, to approximately estimate the value of k_{13} ($\sim 10^4 M^{-1} s^{-1}$). The concentration of $Cu(OAc)_2$ remains unchanged during the reaction, because the $Cu(I)$ salt formed according to eq 14 is rapidly reoxidized to $Cu(II)$ by t -BuOOH. The value of k_{13} is just a rough estimate, since the equilibrium of eq 9 during the reaction is not known, but it appears to be considerably higher than the value of k_{-13} ($\sim 10^{-4} M^{-1} s^{-1}$),¹⁸ which is the key propagation step in the autoxidation chain. The absolute rate constant for hydrogen abstraction from H_2O_2 by methyl radical, determined by a radiolytic procedure, was recently²⁰ reported. The value, $2.7 \times 10^4 M^{-1} s^{-1}$, is quite close to that evaluated in this paper for hydrogen abstraction from t -BuOOH by a primary alkyl radical. Recently, it has been

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Table 3. Reductive Perfluoroalkylation of Alkenes by R_fI and t -BuOOH

alkene	R_fI	yields (%) ^a
cyclohexene	C_4F_9I	85
cyclohexene	$C_8F_{17}I$	73
1-hexene	C_4F_9I	77
1-hexene	$C_8F_{17}I$	72
1-octene	C_4F_9I	73
1-octene	$C_8F_{17}I$	71
3,3-dimethyl butene-1	C_4F_9I	83
3,3-dimethyl butene-1	$C_8F_{17}I$	86

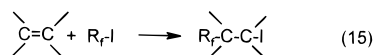
^a Yields based on R_fI .

shown²¹ that the rates of hydrogen abstraction from t -BuOOH can be considerably affected by solvents which form hydrogen bonds with the hydroperoxide; this solvent effect could also influence eq 13.

Apart from the mechanistic implications, these results indicate that the free-radical reduction of primary and secondary alkyl iodides by t -BuOOH in AcOH solution represents a simpler and cheaper methodology compared to the well-known reduction by metal hydride radical chains (eqs 2 and 5). Moreover, the same reaction in the presence of a catalytic amount of a Cu(II) salt represents a new method for the synthesis of alkenes from alkyl iodides, alternative to the classical nucleophilic elimination.

Reductive Alkylation of Alkenes by Perfluoroalkyl and α -Cyanomethyl Radicals. The reductive alkylation of alkenes by perfluoroalkyl iodides according to the classical tin hydride methodology (eqs 3 and 4) is not feasible, owing to the higher rate constants ($\sim 10^8 M^{-1} s^{-1}$ at 25 °C)⁷ for hydrogen abstraction by perfluoroalkyl radicals from Bu_3SnH , which therefore favorably competes with the addition to alkenes ($\sim 10^6 M^{-1} s^{-1}$ at 20 °C);^{7,22} Et_3SiH could work better for such addition reactions of R_f^* to alkenes.²³

We have obtained the reductive perfluoroalkylation of the alkenes by refluxing R_fI , alkene, and t -BuOOH in acetic acid. The results are reported in Table 3. The mechanism initially involves the radical chain addition of R_fI to the alkene (eq 15). The adduct is then reduced as previously described for alkyl iodides. This interpretation is confirmed by the fact that perfluoroalkyliodination of the alkene is mainly observed in the presence of catalytic t -BuOOH. By using excess t -BuOOH and by analyzing the products during the course of the reaction, we obtain the results shown in Figure 4, which support this mechanism.

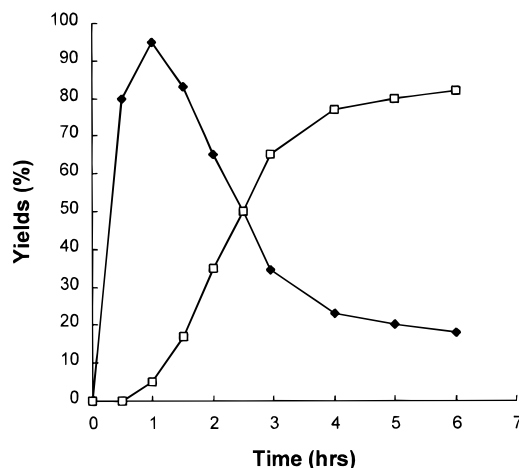


We have observed a similar behavior (reductive alkylation) in the reaction of iodoacetonitrile with alkenes under the same conditions (Table 4). Also in this case, the reductive alkylation of alkenes by the traditional R_3SnH procedure is not feasible because the rates of addition of cyanomethyl radical to alkenes ($10^3\text{--}10^4 M^{-1} s^{-1}$ at room temperature)⁵ are much lower than the rate of hydrogen abstraction from $H-SnBu_3$ ($> 10^6 M^{-1} s^{-1}$ at room temperature). The reaction is characterized, as for

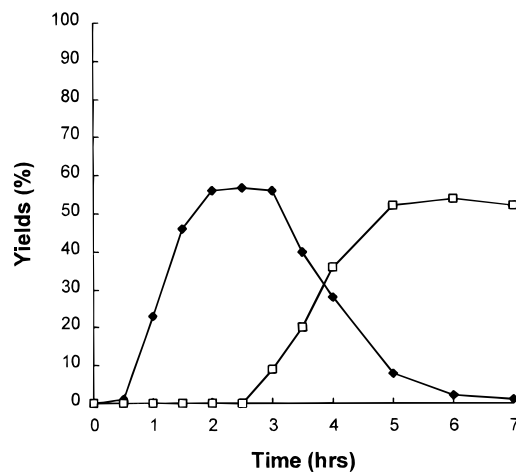
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(23) We thank a reviewer for this suggestion.

**Figure 4.** Reaction of 1 mmol of C_4F_9I with 2 mmol of 1-octene and 2 mmol of t -BuOOH in 10 mL of refluxing AcOH: (◆) $C_4F_9-CH_2-CHI-C_6H_{13}$ and (□) $C_4F_9-C_8H_{17}$.**Table 4.** Reductive Cyanomethylation of Alkenes by $I-CH_2CN$ and t -BuOOH

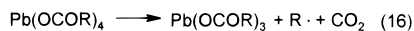
alkene	yields (%) ^a
cyclohexene	42
1-hexene	61
1-octene	59
3,3-dimethyl butene-1	76

^a Yields based on $I-CH_2CN$.**Figure 5.** Reaction of 1 mmol of $I-CH_2CN$ with 10 mmol of 3,3-dimethyl-1-butene and 2 mmol of t -BuOOH in 10 mL of refluxing AcOH: (◆) $(CH_3)_3C-CHI-(CH_2)_2-CN$ and (□) $(CH_3)_3C-(CH_2)_3-CN$.

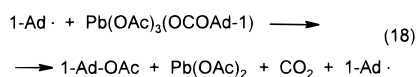
R_fI , by the initial free-radical chain addition of iodoacetonitrile to the alkene, followed by reduction of the adduct according to eq 13, as the results in Figure 5 indicate. Yields are higher with 3,3-dimethylbutene-1 than with the isomers 1-hexene and cyclohexene; this is due to the fact that some allylic attack also occurs (3-iodocyclohexene is formed as a byproduct from cyclohexene) and to a partial intramolecular nucleophilic substitution of the iodine in the initial adduct, $NC-CH_2-CH_2-CHI-R$, which is affected by the steric effect of R, leading to γ -lactones and lactams. By using, under the same conditions, $I-CH_2COOEt$ instead of $I-CH_2CN$, γ -lactones were the only reaction products and no reductive alkylation was observed.

Reductive Alkylation of Electron-Poor Alkenes by Alkyl Radicals Generated from Carboxylic Acids and $Pb(OAc)_4$. The oxidative decarboxylation of carboxylic acids represents a

general, useful, and versatile methodology for generating alkyl radicals.²⁴ Among several processes available for synthetic



purposes, the decarboxylation by Pb(OAc)_4 is sometimes useful. Reaction 16 is generally poorly efficient because it is a slow process, while reaction 17 is extremely fast and the overall reaction becomes a good source of synthetically useful alkyl radicals when a redox chain can be established, in which reaction 16 only acts as the chain initiation step. This occurs when the radical $\text{R}\cdot$ has a marked nucleophilic character, as in the case of 1-adamantyl radical, which has a particularly low redox potential and it is efficiently oxidized by Pb(IV) carboxylate (eq 18) generating a redox chain.²⁵ Similar, excellent, synthetic



results can be obtained when the alkyl radical $\text{R}\cdot$, though not markedly nucleophilic, can give rise to more strongly nucleophilic radicals by reaction with other substrates. This is the case for the reaction of alkyl radicals with protonated heteroaromatic bases, in which the oxidation of strongly nucleophilic radical intermediates generates a highly efficient and selective chain process.²⁶

Extensive kinetic investigation by Fischer and co-workers⁵ has shown that alkyl radicals add rapidly to alkenes conjugated to electron-withdrawing groups ($\text{X} = \text{COR}, \text{COOR}, \text{CN}, \text{etc.}$) and that the polar effect plays an essential role in this addition. The radical adduct, however, has electrophilic character and cannot give rise to redox chain by a reaction with Pb(IV) similar to eq 18. In fact, the oxidation of carboxylic acids by Pb(OAc)_4 in the presence of electron-poor alkenes, such as maleic anhydride, ethyl maleate, and fumarate in several solvents (carboxylic acids, alkanes, chloroalkanes, acetonitrile, esters, ketones) gives only poor conversion (<5%) for the reductive alkylation of the alkene, indicating that even if the radical adduct abstracts a hydrogen atom from the solvent (S-H), the resulting radical ($\text{S}\cdot$) does not have enough nucleophilic character to sustain chain processes. However, by utilizing solvents, such as THF or cumene, which generate more nucleophilic radicals by hydrogen abstraction, we obtained much better results for the reductive alkylation, as reported in Table 5. THF was mostly utilized for two main reasons: hydrogen abstraction from THF by electrophilic radicals is relatively fast for both enthalpic and polar effects (eq 19) and the resulting radical has a particularly marked nucleophilic radical with a low oxidation potential, which makes the oxidation by Pb(IV) carboxylate (eq 20) very fast. The overall stoichiometry of the reaction is shown by eq 21. It represents an alternative synthetic method to the classical reductive alkylation by alkyl halides and tin hydrides. To the best of our knowledge eq 21 represents the only procedure, known so far, for the direct use of carboxylic acids as sources of alkyl radicals suitable for the reductive alkylation of alkenes.

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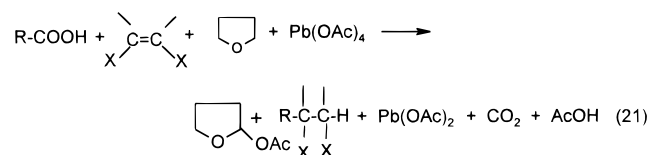
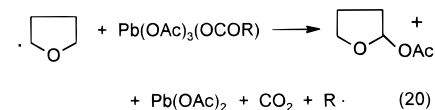
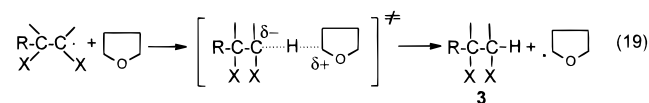
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Table 5. Reductive Alkylation of Alkenes According to Eq 21

R	procedure	yields (%) ^a		
		maleic anhydride	ethyl fumarate	ethyl maleate
<i>n</i> -Pr	A	58.1	47.7	46.5
<i>n</i> -Pr	B	52.1	38.8	44.3
<i>i</i> -Pr	A	81.0	73.5	80.0
<i>i</i> -Pr	B	68.2	63.4	72.7
<i>i</i> -Pr ^b	A	65.4	56.2	47.8
<i>n</i> -Bu	A	61.3	48.7	52.4
<i>n</i> -Bu	B	51.8	27.8	40.0
<i>i</i> -Bu	A	79.4	61.2	68.3
<i>t</i> -Bu	A	49.2	42.0	62.2
cyclohexyl	A	85.0	68.1	62.2
cyclohexyl ^b	A	62.8	54.2	51.6
1-adamantyl	A	88.0	77.2	70.5
benzyl	A	51.8	37.5	
<i>p</i> -Cl-benzyl	A	53.9	39.0	

^a Based on Pb(OAc)_4 . ^b Cumene was used as solvent.

The key step, which makes the redox chain particularly efficient, is the fast and selective oxidation of the α -THF \cdot radical by Pb(IV) carboxylate (eq 20).



The addition of α -THF \cdot radical to the alkene can be a competitive process, particularly for the most reactive alkenes, such as maleic anhydride. This side reaction can be minimized by keeping the stationary concentration of the alkene low by slowly dropping it in the reacting solution.

Conclusion

New methods for free-radical iodination of alkanes, reduction of alkyl iodides, reductive perfluoroalkylation, and cyanomethylation of simple electron-rich alkenes by *t*-BuOOH and reductive alkylation of electron-poor alkenes by Pb(OAc)_4 have been developed. The paradox of these new syntheses concerns the use of strong oxidants for reductive processes. The importance of the polar effects and of the knowledge of the absolute rate constants of many of the involved elementary steps has been emphasized. Evidence of hydrogen abstraction from *t*-BuOOH by alkyl radicals (the reversed key step of the autoxidation) and an approximate evaluation of its rate constant are reported.

Experimental Section

Materials and Methods. All reagents were purchased from Aldrich. Mass spectra were performed on a GLC-MS instrument, using a gas chromatograph equipped with SBP-1 fused silica column (30 m \times 0.2 mm i.d., 0.2 μm film thickness) and helium as carrier gas. GLC analyses were performed on a capillary gas chromatograph equipped with a SBP-5 fused silica column (25 m \times 0.25 mm i.d., 1 μm film thickness)

at a hydrogen flow rate of $8 \text{ cm}^3 \text{ min}^{-1}$, PTV injector, flame ionization detector. ^{19}F NMR spectra were registered on a spectrometer operating at 235 MHz. Chemical shifts are referenced to internal CFCl_3 . Proton NMR spectra with ^{19}F broadband decoupling were acquired using a supplementary frequency synthesizer.

Iodination of Cyclohexane by $n\text{-C}_4\text{F}_9\text{I}$. (A) A solution of 1 mmol of $n\text{-C}_4\text{F}_9\text{I}$, 5 mL of AcOH, and 5 mL of cyclohexane was warmed at 80°C with variable amounts of $t\text{-BuOOH}$, as indicated in Figures 1 and 2. The yields of cyclohexyl iodide were determined by GLC using 2-iodoheptane as internal standard. The results are reported in Figures 1 and 2. (B) A solution of 1 mmol of $n\text{-C}_4\text{F}_9\text{I}$ and 1 mmol of $t\text{-BuOOH}$ in 9 mL of AcOH and 1 mL of cyclohexane was warmed at 100°C and the yields of cyclohexyl iodide were determined during the course of the reaction as in procedure A. The results are reported in Figure 3. The formation of *tert*-butyl peracetate has been qualitatively revealed during the reaction by a GLC comparison with an authentic sample.

Reduction of Iodocyclohexane and 1-Iodododecane by $t\text{-BuOOH}$. Alkyl iodide (1 mmol) and 2 mmol of $t\text{-BuOOH}$ in 10 mL of AcOH were refluxed and the yields of the alkyl iodides, cyclohexane, and dodecane were determined during the course of the reaction by GLC with *n*-decane as internal standard. 85–87% yields of alkanes were obtained under the best conditions. Minor amounts (<10%) of cyclohexanol and 1-dodecanol were revealed by GLC. The reaction of 1-iodododecane with variable amounts of $t\text{-BuOOH}$ was carried out under the same conditions and the ratios between *n*-dodecane and 1-dodecene were determined by GLC. The results are reported in Table 1. Also in this case, the formation of *tert*-butyl peracetate has been qualitatively revealed by GLC.

Reaction of 1-Iodododecane with $t\text{-BuOOH}$ in the Presence of $\text{Cu}(\text{OAc})_2$. The reaction was carried out as above with variable amounts of $t\text{-BuOOH}$ and $\text{Cu}(\text{OAc})_2$, as reported in Table 2. The relative amounts of *n*-dodecane and 1-dodecene were determined by GLC, by using *n*-decane as internal standard, and the overall peroxide was determined by iodometric titration. The experiment of Table 2 involving 3 mmol of $t\text{-BuOOH}$ was analyzed when 20% of $t\text{-BuOOH}$ had reacted and the results were utilized for an approximate evaluation of k_{13} ($\sim 10^4 \text{ M}^{-1} \text{ s}^{-1}$).

Reductive Perfluoroalkylation of Alkenes by $n\text{-C}_4\text{F}_9\text{I}$, $n\text{-C}_8\text{F}_{17}\text{I}$ and $t\text{-BuOOH}$. Alkene (2 mmol), 1 mmol of perfluoroalkyl iodide, and 2 mmol of $t\text{-BuOOH}$ in 10 mL of AcOH were refluxed for 6 h. The solutions were directly analyzed by GLC-MS, which revealed the expected molecular ions, and by ^{19}F NMR spectra. The absolute yields were determined by ^{19}F NMR, using tetrafluoro-*p*-benzoquinone as internal standard (signal at -142.5 ppm relative to CFCl_3). The products of reductive perfluoroalkylation obtained by $\text{C}_4\text{F}_9\text{I}$ give four ^{19}F NMR singlet signals at -119.1 to -119.5 , -123.0 to -123.3 , -127.2 to -127.5 , and -82.1 to -82.4 ppm, respectively, for CF_2 in the α , β ,

and γ positions and for CF_3 . The products of reductive perfluoroalkylation by $\text{C}_8\text{F}_{17}\text{I}$ give signals at -110.4 to -110.8 (CF_2 in position 1), -117.6 to -118.2 (3 CF_2 in positions 2, 3 and 4), -119.2 to -119.4 (CF_2 in position 5), -119.8 (CF_2 in position 6), -122.5 (CF_2 in position 7), and -77.7 (CF_3) ppm. The results are reported in Table 3. The intermediate adducts of R_fI to alkenes, $\text{R}_f\text{-CH}_2\text{-CH}_2\text{-CHI-R}$, were identified by comparison (GLC-MS) with authentic samples prepared by known procedures.²⁷ The analyses carried out during the reaction (Figure 4) revealed that the iodoadduct is initially formed and then converted into the reduced product.

Reductive Cyanomethylation of Alkenes by $\text{I-CH}_2\text{CN}$ and $t\text{-BuOOH}$. Alkene (10 mmol), 1 mmol of $\text{I-CH}_2\text{CN}$, and 2 mmol of $t\text{-BuOOH}$ in 10 mL of AcOH were refluxed for 8 h. The reaction products were analyzed by GLC and GLC-MS and identified by comparison with authentic samples. The results are reported in Table 4. The analyses carried out during the reaction (Figure 5) revealed that the iodoadduct is initially formed and then converted into the reduced product. Allyl iodides, γ -lactones, and γ -lactams are byproducts of the reaction. Experiments with the iodoadducts, $\text{NC-CH}_2\text{-CH}_2\text{-CHI-R}$, carried out under the same conditions, but in the absence of $t\text{-BuOOH}$, have shown that lactones and lactams arise from intramolecular reactions of the iodoadducts, which compete with the reductive process in the presence of $t\text{-BuOOH}$. The same reactions, carried out with $\text{I-CH}_2\text{-COOEt}$ instead of $\text{I-CH}_2\text{CN}$, and with $t\text{-BuOOH}$, only gave γ -lactones and no product of reductive alkylation.

Reductive Alkylation of Alkenes by Carboxylic Acids and $\text{Pb}(\text{OAc})_4$. Maleic anhydride, ethyl fumarate, and ethyl maleate were utilized as alkenes.

Procedure A: A solution of 7 mmol of the alkene in 10 mL of THF was dropped within 2 h to a refluxing solution of 5 mmol of $\text{Pb}(\text{OAc})_4$ and 5 mmol of carboxylic acid in 20 mL of THF. The solution was refluxed for an additional 30 min, then washed with 10% aqueous HCl and analyzed by GLC, using ethyl succinate as internal standard. All the reaction products were identified by comparison (GLC-MS) with authentic samples obtained by the known¹ procedure from alkyl iodide and $n\text{-Bu}_3\text{SnH}$.

Procedure B: A solution of carboxylic acid (5 mmol), $\text{Pb}(\text{OAc})_4$ (5 mmol) and alkene (10 mmol) in 20 mL of THF was refluxed for 2 h. The analysis was carried out as in procedure A and the results are reported in Table 5.

Acknowledgment. This work is dedicated to Prof. Keith U. Ingold on the occasion of his 70th birthday.

JA9904179

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