Thermolysis of *N*-tetramethylpiperidinyl esters: homolytic fragmentation and induced decomposition

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Dedicated to Professor Nouria A. Al-Awadi on the occasion of her 55th birthday, and in recognition of her contributions to high temperature chemistry

Abstract

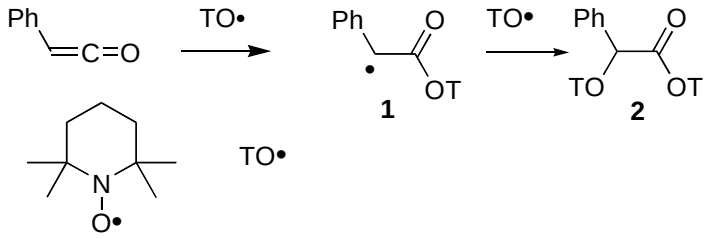
The esters PhCH(OT)CO_2T (**2**), $PhCH_2CO_2T$ (**5**), $PhCO_2T$, (**6**), and 1-$AdCO_2T$ (**7**, Ad = 1-adamantyl), T = 2,2,6,6-tetramethyl-*N*-piperidinyl, undergo thermal decomposition at 120 °C in toluene with the formation of carboxylic acids, 2,2,6,6-tetramethylpiperidine (TH), and bibenzyl in all cases, indicative of the formation of 2,2,6,6-tetramethylpiperidinyl radicals, but excluding the formation of the radicals $PhCH_2CO_2$• and 1-$AdCO_2$•. Qualitative kinetic measurements show that **5-7** react much faster than expected for rate-limiting bond-homolysis, suggesting the occurrence of induced decomposition. Addition of 2,6-di-*tert*-butyl-4-methylphenol (BHT) to the reaction of $PhCH_2CO_2T$ in hexane accelerates the reaction, with a first-order dependence on [BHT], and leads to the formation of the characteristic dimers **9** and **10** from 2,6-di-*tert*-butyl-4-methylphenoxyl radical (**12**). These reactions of the esters **5-7** are interpreted to occur by molecule-induced homolysis, in which a hydrogen atom from toluene or BHT is transferred to oxygen forming RCO_2H and the 2,2,6,6-tetramethylpiperidinyl radical T• in a concerted process. Comparable behavior is observed for reactions in chloroform. PhCH(OT)CO_2T (**2**) is proposed to form an intermediate PhCH(•)CO_2T (**1**) which gives α-lactone **19**. Density functional calculations are used to model the overall energy changes in these reactions.

Keywords: TEMPO ester, free radicals, induced decomposition, molecule induced homolysis

Introduction

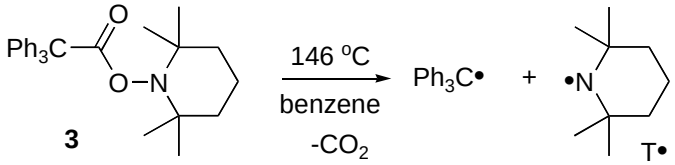
The thermal stability and other properties of adducts of tetramethylpiperidinyloxyl (TEMPO, TO•) and related aminoxyl radicals have become of great interest[1,2] because of their role in living free radical polymerization,[3] and other applications. In our studies of the reactions of free radical reactions of ketenes,[4] we have found that 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO, TO•)

reacts with ketenes such as PhCH=C=O to form 1,2-diaddition products. This reaction was shown to proceed by radical attack of TO• at the carbonyl carbon forming enolic radical **1**, which was then trapped by a second TEMPO to form **2** (Scheme 1). With other ketenes the initial enolic radicals may react by rearrangement, dimerization, or capture by oxygen, depending on the structure.[4]



Scheme 1

Esters of 2,2,6,6-tetramethyl-*N*-hydroxypiperidine (TOH) are formed in these reactions, and the thermal behavior of such esters[1f,4d,e,5a] as well as the chemistry of the derived ester enolates[1b-d] and of *N*-acyloxy imines[5b] have been of interest in several laboratories. We have examined the reactivity of *N*-2,2,6,6-tetramethylpiperidinyl triphenylacetate (**3**),[4e] and found this undergoes first order decomposition in benzene forming products derived from triphenylmethyl radical and from 2,2,6,6-tetramethylpiperidinyl radical (T•), consistent with rate-limiting concerted two-bond cleavage (Scheme 2).[4e] This reaction is slower than the corresponding concerted two-bond cleavage of the structurally analogous peroxy ester Ph_3CCO_3Bu-*t* by a factor of 10^8, and cleavage of the N-O bond as indicated by these experiments is computed for HCO_2T to be 7.8 kcal/mol more favorable than the alternative C-O bond cleavage.[4e]

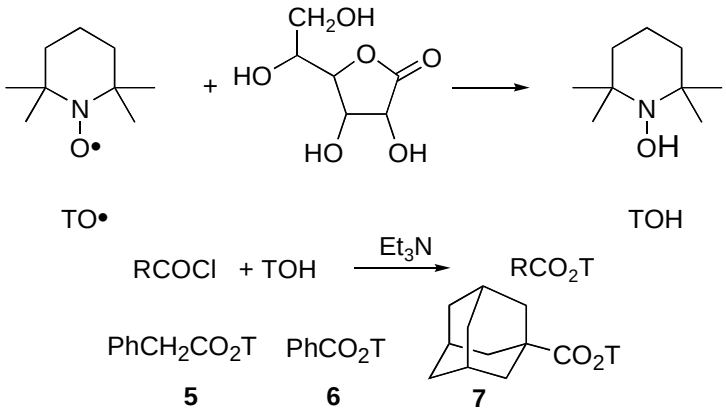


Scheme 2

The ester *t*-$BuCO_2T$ (**4**) was reported to distill at 150 °C without apparent decomposition,[5a] and this thermal stability is expected based on the demonstrated low reactivity of **3**.[4e] Similarly $PhCH_2CO_2T$ (**5**) was reported to decompose with a rate constant in *tert*-butylbenzene of 1.1 x 10^{-9} s^{-1} at 150.8 °C,[1f] corresponding to a half-life of 20 years. However we have observed that in solvents such as toluene and chloroform that **5** and related esters surprisingly appeared to be significantly more reactive than found for such esters in other media. These unexpected results prompted a detailed study of the reactivity of these substrates, as reported herein.

Results

2,2,6,6-Tetramethylpiperidinol (TOH) was prepared by ascorbic acid reduction of TEMPO.[1f,5a] The ^{1}H NMR spectrum of TOH was not fully resolved at room temperature, but at –60 °C and 500 MHz separate signals for the axial and equatorial methyl groups were observed at δ 1.10 and 1.18. 2,2,6,6-Tetramethyl-*N*-piperidinyl esters **5**-**7** were obtained by the reaction of the appropriate acyl chlorides with TOH (Scheme 3).



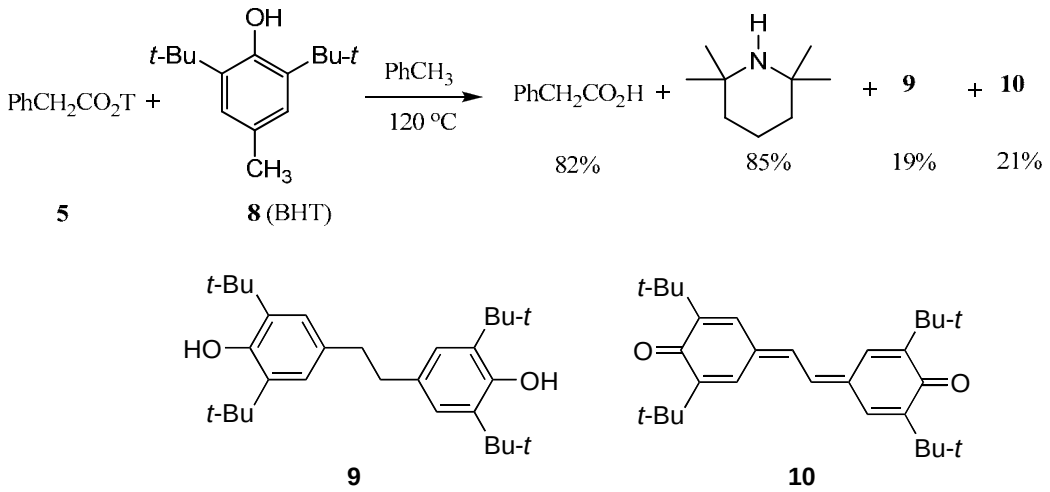
Scheme 3

The substrates **5**-**7** showed no significant reaction on heating in either carbon tetrachloride or cyclohexane in sealed tubes for 10 day at 130-135 °C. However reaction did occur in other solvents, and products from the thermolysis of **2** and **5**-**7** in degassed toluene or $CDCl_3$, were determined by first extracting by base and acidifying to separate the acidic products, which were collected. The volatile products were identified and quantitatively analyzed by comparison of their gas chromatographic and mass spectral behavior with those of authentic materials. Product yields are reported in Table 1.

Table 1. Product yields (%, mol/mol) from thermolysis of esters RCO_2T (**2** and **5**-**7**) in toluene and $CDCl_3$

R	**$PhCH_2$**	**Ph**	**1-Ad**	**$PhCH_2$**	**Ph**	**1-Ad**
T (°C)	120	120	120	120	120	100
Solvent	$PhCH_3$	$PhCH_3$	$PhCH_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$
Time (h)	118	24	20	24	15	14
$RCO_2H(D)$ (%)	88	78	73	84	91	81
TH(D) (%)	78 ±3	81 ±2	74 ±1	97 ±1	95 ±2	98 ±1
RCO_2Bn (%)	29 ±3	14 ±3	8 ±2			
BnOT (%)	14 ±2	11 ±2	14 ±2			
$(Bn)_2$ (%)	40 ±2	20 ±3	37 ±3			
CCl_4 (%)				42 ±1	38 ±2	24 ±2
C_2Cl_6 (%)				14 ±3	10 ±2	20 ±2

The addition of one equivalent of 2,6-di-*tert*-butyl-4-methylphenol (BHT, **8**) to **5** in toluene accelerated the decomposition at 130-135 °C, and led to the formation of $PhCH_2CO_2H$, tetramethylpiperidine, and the known[5d] dimerization products **9** and **10** derived from BHT (Scheme 4).



Scheme 4. BHT reaction with Tempo ester **5**.

Attempts to measure the kinetics of the reaction of esters **5-7** in toluene or chloroform at 120 °C by observation of the decrease of the ester carbonyl absorption in the infrared, or of the changes in the ^{1}H NMR in deuterated solvents, gave irregular results and apparent induction periods were observed in many of the reactions. The reactions showed approximate first-order dependences on [RCO_2T], but reliable rate constants were not obtained. The half-lives of **5-7** in toluene at 120 °C were similar, in the range 2-3 h, while half-lives in $CHCl_3$ were less by factors of 3-4.

The reaction of **5** in hexane with added BHT at 120 °C with measurement of the decrease in the ester carbonyl absorption by IR however gave a greatly accelerated reaction with good first order kinetics, and a linear dependence on the concentration of BHT. The measured rate constants are given in Table 2, and the dependence of the observed rate constant on the concentration of BHT is shown in Figure 1). These gave a derived second order rate constant k_2 = (3.03 ±0.27) x 10^{-4} M^{-1} s^{-1}.

Table 2. Rate constants at 120 °C for reaction of $PhCH_2CO_2T$ in hexane versus [BHT]

[BHT] (M)	0.41	1.00	1.52	1.71
k (s^{-1} x10^{-4})	1.00 ±0.04	2.60 ±0.24	4.09 ±0.35	5.08 ±0.10

Ester **5** in isooctane with 2 equivalents of 2,2,6,6-tetramethypiperidin-1-ol (TOH) reacted at 120 °C forming phenylacetic acid, tetramethylpiperidine, and TEMPO (Scheme 5).

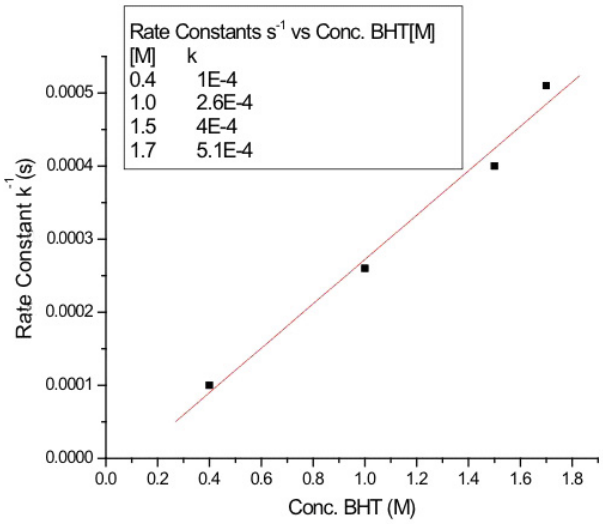
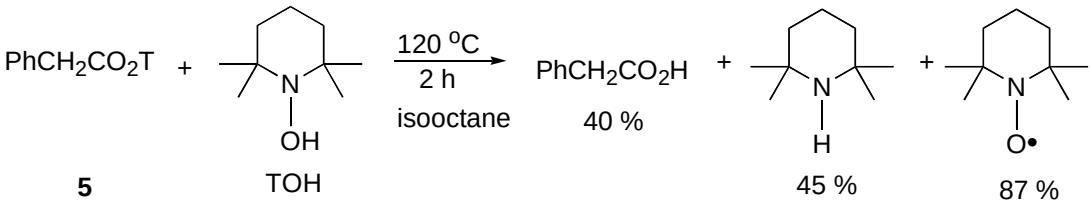
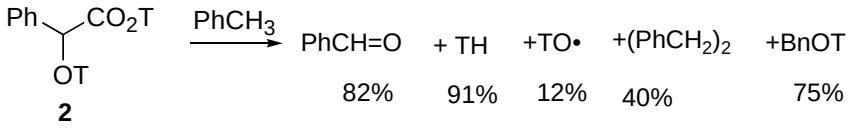


Figure 1. Dependence of rate constants for reaction of $PhCH_2CO_2T$ at 120 °C in hexane versus [BHT].



Scheme 5

Thermolysis at 100 °C of the bis(TEMPO) adduct **2** of phenylketene in toluene gave benzaldehyde (82%), 2,2,6,6-tetramethylpiperidine (TH, 91%), bibenzyl (40%), TEMPO (TO•, 12%), and *N*-benzyloxy-2,2,6,6-tetramethylpiperidine ($PhCH_2OT$, 75%, Scheme 6).



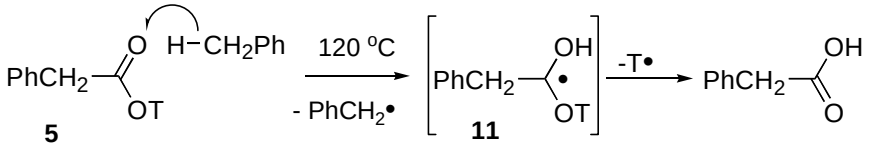
Scheme 6

Discussion

The reactions of the esters **5-7** in toluene at 120 °C giving TH, bibenzyl, and benzyl esters (Table 1) demonstrate that piperidinyl radicals T• and benzyl radicals are being generated. However carboxyl radicals $PhCH_2CO_2$• and 1-$AdCO_2$• are known to undergo rapid

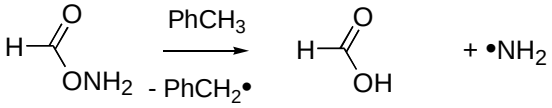
decarboxylation under these conditions,[6] and so the high yields of the corresponding acids observed must arise from other sources.

A plausible mechanism for these reactions involves molecule induced homolysis, in which toluene transfers a hydrogen atom to **5** with either formation of an intermediate radical **11** which then cleaves to the acid and a piperidinyl radical, or formation of these products in one step (Scheme 7). This process explains the formation of carboxylic acids without the generation of the corresponding carboxylate radicals, while at the same time accounting for the formation of the tetramethylpiperidinyl radical and the products derived from it.



Scheme 7

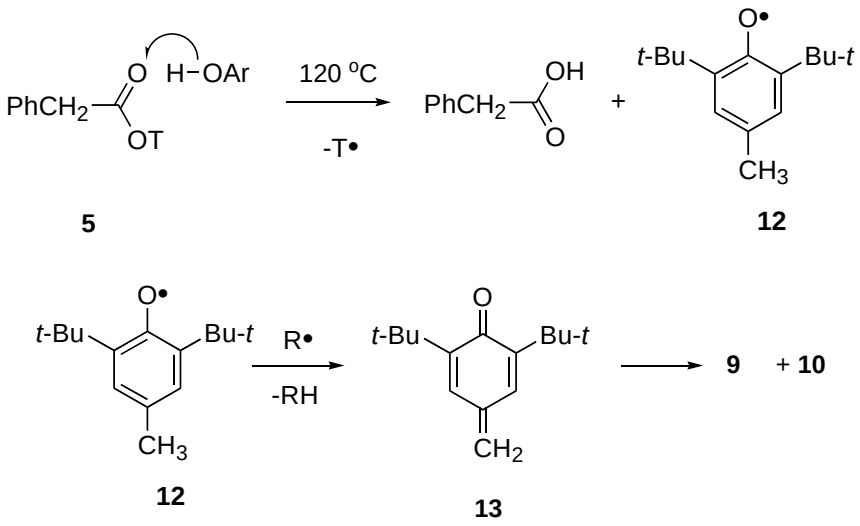
Computations at the B3LYP/6-311++G**//B3LYP6-311++G** level using Gaussian 98[7] indicate that ΔE for hydrogen atom transfer from toluene to formyloxyamine ($HCONH_2$) is endothermic by 68.0 kcal/mol, and so this step would be greatly disfavored. However direct formation of formic acid and NH_2• is more favorable, and is endothermic by 27.8 kcal/mol (Scheme 8). Previous work[4e] also showed that cleavage of HCO_2T to HCO_2• and T• is favored by entropy, with ΔG 10.0 kcal/mol more favorable than the cleavage of HCO_2NH_2 to HCO_2• and NH_2•. The process of Scheme 7 would be irreversible as the T• radicals are scavenged by toluene, and appears to be energetically feasible at 120 °C, so this pathway with concerted formation of T• from **5** upon reaction with toluene is favored. Efforts to calculate a structure for a transition state for hydrogen transfer to $HCONH_2$ from toluene were unsuccessful, and so an estimate of the barrier for this process is not available.



Scheme 8

Further evidence for the mechanism of Scheme 7 comes from the use of different hydrogen atom donors of known X-H bond strengths.[8] Addition of 2,6-di-*tert*-butyl-4-methylphenol (BHT) results in an acceleration of the reaction, with a linear dependence on [BHT] (Fig 1) and formation of phenylacetic acid, tetramethylpiperidine, and the dimers **9** and **10** from in high yield (Scheme 4). Similarly the reaction is also promoted by the addition of 2,2,6,6-tetramethypiperidin-1-ol (TOH) (Scheme 5). The known BDE of toluene,[8b] chloroform,[8c] BHT,[8e,f] and TOH[8d] are 89.9, 93, 81.0, and 69.6 kcal/mol, respectively, and are consistent with the more facile reactions of **5** with TOH and BHT.

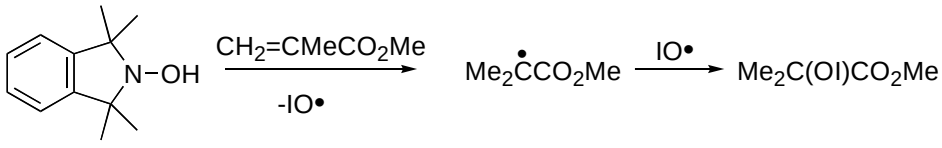
The reaction of **5** with BHT is similarly indicated to occur with hydrogen atom transfer from BHT forming aryloxy radical **12** and phenylacetic acid directly by a concerted pathway, followed by further hydrogen abstraction from **12** and formation of the dimeric products by the known conversion of **12** to the quinone methide **13** and further reaction (Scheme 9).



Scheme 9

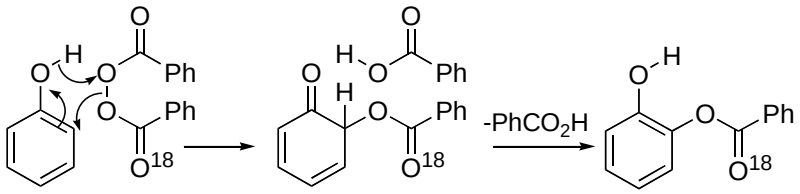
The reactions in $CDCl_3$ for **5**-**7** result in a high efficiency for formation of the corresponding carboxylic acids and tetramethylpiperidine (Table 1), and can be explained by a deuterium atom transfer process analogous to that of Scheme 7, with formation of the carboxylic acid, CCl_3•, and tetramethylpiperidinyl radical (T•). The latter then abstracts hydrogen from chloroform forming tetramethylpiperidine and another CCl_3•, which would lead to C_2Cl_6. The formation of CCl_4 could result from abstraction of a chlorine atom by CCl_3• from $CDCl_3$, as has been observed in sonication of $CHCl_3$ in water.[8g]

Radical induced decomposition of free radical initiators has long been known,[9a] while radical generation by reaction of non-radical species (molecule induced homolysis), is also well documented.[9b-e] Precedent for radical initiation by hydrogen atom transfer is found in the reaction of 2-hydroxy-1,1,3,3-tetramethyl-1,3-dihydroisoindole (**14**, IOH) reacting with methyl methacrylate, proposed[9e] to react via the radical **15** and IO• leading to the product **16** (Scheme 10).



Scheme 10

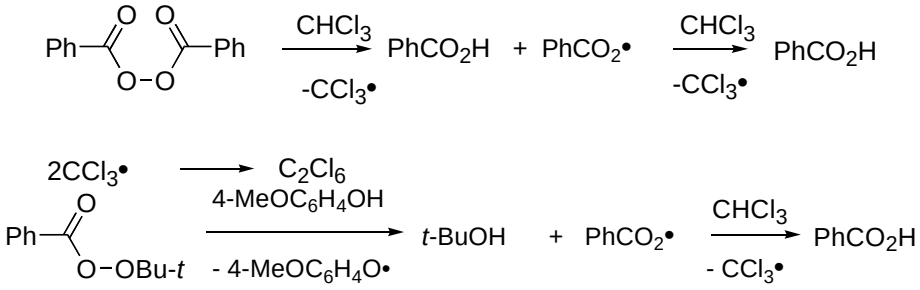
Phenols are known to react with benzoyl peroxide forming 2-benzoyloxyphenols **17** in a process that can be depicted as proceeding through an electrocyclic process (Scheme 11) or a stepwise variant.[9b,c] Evidence for this mechanism included the first order dependence of the reaction rate on both phenol and benzoyl peroxide concentrations, a kinetic isotope effect for the phenolic hydrogen k_H/k_D = 1.32, rate acceleration in polar solvents and retardation in hydrogen bonding solvents, rate accelerations by substituents on the phenol except for retardations by bulky *ortho* substituents, and predominant retention in the carbonyl oxygen of **17** of ^{18}O label originally present in the carbonyl oxygen of the benzoyl peroxide.[9b,c]



17

Scheme 11

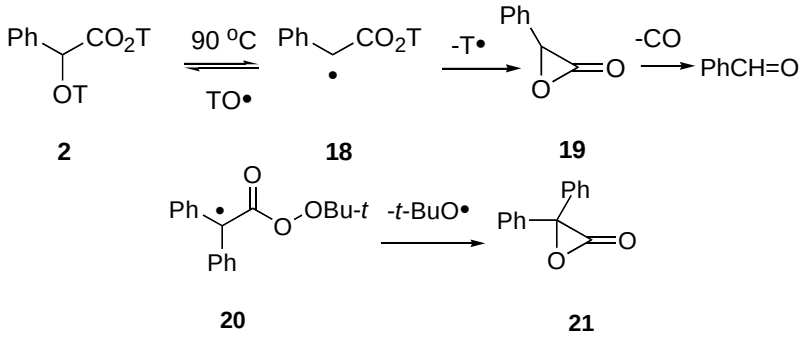
Benzoyl peroxide reacts in $CHCl_3$ at 80 °C to form benzoic acid (85%) and hexachloroethane (54%),[9b] a reaction which can be explained as involving hydrogen atom transfer from $CHCl_3$ (Scheme 12). *tert*-Butyl perbenzoate reacts with 4-methoxyphenol in $CHCl_3$ at room temperature to give benzoic acid (93%) and *tert*-butyl alcohol (81%),[9b] and this reaction can also be explained by hydrogen atom donation from the phenol (Scheme 12).



Scheme 12

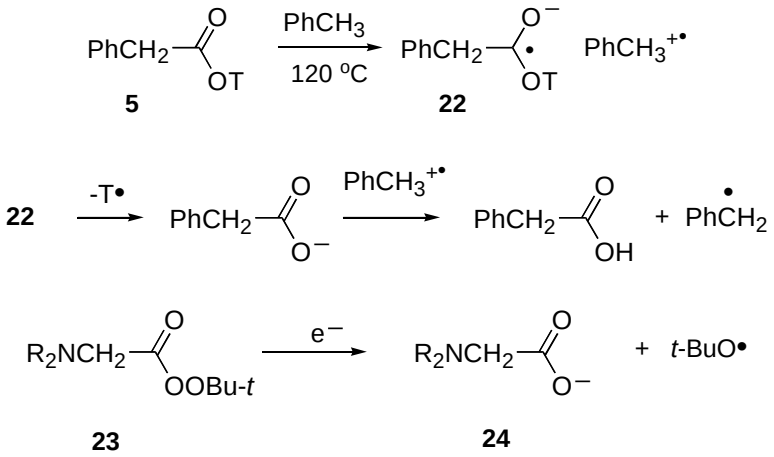
Thermolysis of the bis(TEMPO) adduct **2** (Scheme 6) is expected[1g] to proceed through the reversible dissociation of a TEMPO radical from the α-position forming the radical **18**, which is a known reaction of such α-TEMPO substituted esters.[1g,4d] The formation of 2,2,6,6-tetramethylpiperidinyl radicals (T•) could occur with conversion of **1** to an α-lactone intermediate **19**, which upon decarbonylation would give benzaldehyde (Scheme 13). α-Lactones have long been established as reactive intermediates that in rare cases have been directly observed, and are known to undergo thermal decarbonylation.[10] Precedent for formation

of an α-lactone from a structually analogous peroxy ester with an adjacent radical site is shown (Scheme 13).[10a] Formation of the other radical products would result from hydrogen atom abstraction by T• from toluene forming TH and benzyl radicals, and the benzyl radicals could combine to form bibenzyl, or react with TO• to give $PhCH_2OT$.



Scheme 13

An alternative mechanism that can be considered is an electron transfer process from toluene to an ester such as **5** forming the radical anion **22** which could fragment upon generation or in a separate step to form a carboxylate anion and the piperidinyl radical T• (Scheme 14). The carboxylate radical could then react with the toluene radical cation formed in the first step to form the carboxylic acid and a benzyl radical. Precedent for this step lies in the electrochemical cleavage of the peroxy ester **23**, which upon electrochemical reduction forms the carboxylate anion **24** and *t*-butoxy radical in a concerted step.[11a]



Scheme 14

However the measured reduction potential of **5** is about -1 eV, whereas the oxidation potential of toluene is 3 eV,[11b] and so this electron transfer appears improbable. We also found that mesitylene, which has an appreciably lower oxidation potential than toluene (2.35 V),[11b] did not noticeably enhance the reactivity of **5** compared to the reaction in toluene, and this also argues against this possibility. The enhancement of the reactivity of **5-7** by the addition of the hydrogen donors BHT and tetramethylpiperidinol also indicate that hydrogen atom donation is the controlling factor in these reactions.

Summary

In summary *N*-tetramethylpiperidinyl esters **5-7** have high thermal stability in alkane solvents, but react within hours at 120 °C in toluene or chloroform, or in alkanes in the presence of added good hydrogen atom donors BHT or tetramethylpiperidinol. Carboxylic acids are major products in all cases, and exclude the formation of carboxylate radicals from **5** or **7**. The results are reasonably explained as occurring by hydrogen atom donation from the solvent or additive forming carboxylic acids and tetramethylpiperidinyl radicals, and this process is likely concerted.

Experimental Section

General Procedures. Chromatography was carried out on silica gel. Gas chromatographic analysis used a Simplicity 5 column (poly-5% diphenyl/95% dimethylsiloxane) with a flame ionization detector. Solutions for TEMPO reactions were degassed and conducted under argon. Authentic samples of $PhCH_2OT$, $PhCH_2T$,[5c] $PhCO_2CH_2Ph$, and $PhCH_2CO_2CH_2Ph$ were prepared for product identification. **Benzyl benzoate.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (s, 2H), 7.34-7.58 (m, 7H), 7.60 (t, *J* = 2.6 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 2H). **Benzyl phenylacetate.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 2H), 5.14 (s, 2H), 7.31-7.36 (m, 10H).

1-Hydroxy-2,2,6,6-tetramethylpiperidine (TOH).[5a] TEMPO (1 g, 6.4 mmol) was added to a solution of ascorbic acid (1.87 g) and KOH (0.42 g) in H_2O (18 mL). at room temperature The resulting suspension was stirred vigorously until the red color of TEMPO disappeared, with formation of a white precipitate (5 min). The mixture was extracted with ether and the ether extract was washed with water and brine, dried over Na_2SO_4, and the solvent removed under reduced pressure to yield 1-hydroxy-2,2,6,6-tetramethylpiperidine, (0.94 g, 94%, pure by ^{1}H NMR). ^{1}H NMR (500 MHz, $CDCl_3$, -60 °C) δ 1.10 (s, 6H), 1.18 (s, 6H), 1.40 (m, 4H), 1.56 (m, 2H), 2.26 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, -60 ^{o}C) δ 16.8, 18.9, 32.2, 39.1, 58.7 (the spectra were not fully resolved at room temperature). IR (pentane) 3590 cm^{-1}. EIMS 157, 156, 142, 109, 83, 69, 55.

***N*-2,2,6,6-Tetramethylpiperidinyl phenylacetate (5).**[1f] Phenylacetyl chloride (20 mmol) was added to a stirred mixture of TOH (20 mmol) and Et_3N (20 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The mixture was stirred 20 min, 2 M HCl (100 mL) was added, and the organic layer was

washed with $NaHCO_3$ (3 x 100 mL) and brine, dried over $NaSO_4$, and concentrated. Chromatography on silica gel with CH_2Cl_2 gave **5** as a colorless oil (84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 6H), 1.03 (s, 6H), 1.35-1.70 (m, 6H), 3.66 (s, 2H), 7.30-7.34 (m, 5H).^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 20.6, 21.1, 31.9, 32.2, 39.2, 40.9, 60.3, 60.6, 127.3, 128.7, 128.8, 129.6, 129.8, 134.3, 171.1 . IR ($CDCl_3$) 1751 cm^{-1}. EIMS 275, 260, 237, 157, 142, 123, 91, 69. HREIMS *m/z* calcd for $C_{17}H_{26}NO_2$ (MH^+) 276.1950, found 276.1964.

***N*-2,2,6,6-Tetramethylpiperidinyl benzoate (6)**[12] was prepared as for **5** from benzoyl chloride in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (s, 6H), 1.28 (s, 6H), 1.45-1.79 (s, 6H), 5.11 (s, 2H), 7.56 (m 2H), 7.61 (m, 1H), 8.10 (d, *J* = 7.1 Hz, 2H).

***N*-2,2,6,6-Tetramethylpiperidinyl 1-adamantanecarboxylate (7).** 1-Adamantylcarbonyl chloride (10 mmol) was added to a stirred mixture of TOH (20 mmol) and Et_3N (20 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The mixture was stirred 20 min, 2 M HCl (100 mL) was added, and the organic layer was washed with $NaHCO_3$ (3 x 100 mL) and brine, dried over $NaSO_4$, and concentrated. Chromatography on silica gel with CH_2Cl_2 gave **7** (88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 6H), 1.17 (s, 6H), 1.40-2.04 (m, 21H).^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 18.0, 25.3, 29.1, 33.9, 36.3, 36.6, 38.3, 57.2, 173.4 . IR ($CDCl_3$) 1748 cm^{-1}. EIMS 319, 304, 279, 163, 156, 142, 135, 107, 93, 79. HREIMS *m/z* calcd for $C_{21}H_{33}NO_2$ 319.2517, found 319.2511.

Benzyl 1-adamantanecarboxylate was obtained from the acyl chloride and benzyl alcohol as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (s, 6H), 1.93 (s, 6H), 2.02 (s, 3H), 5.11 (s, 2H), 7.31-7.36 (m, 5H).^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2, 36.7, 39.1, 41.0, 65.9, 127.9, 128.1, 128.7, 136.8, 177.7. IR ($CDCl_3$) 1716 cm^{-1}. EIMS 270, 163, 135, 107, 91, 77. HREIMS *m/z* calcd for $C_{18}H_{22}O_2$ 270.1628, found 270.1620.

Thermolysis of 2

A solution of **2** (7.3 mg, 0.017 mmol) in $CDCl_3$ (1 mL) in a sealed NMR tube was heated 24 h at 100 °C. The products were identified by ^{1}H NMR and GC/MS as benzaldehyde (68.5 ±1%), tetramethylpiperidine (TH, 94 ±14%), and TEMPO (42.5 ±13.5%).

Heating **2** (15 mg, 0.035 mmol) in toluene (2 mL) 24 h in a sealed ampoule at 100 °C and evaporation of the solvent and analysis by ^{1}H NMR and GC/MS showed benzaldehyde, TH, TEMPO, bibenzyl and BnOT. Chromatography (silica gel, $CHCl_3$) gave BnOT (54%) and bibenzyl (32%). An unidentified product was also separated: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.392-7.322 (m, 5H), 4.721 (s, 2H).

For product studies of **5-7** in toluene and chloroform the ester (20 mg) in an ampoule with the solvent was degassed for 5 min, and the ampoule was sealed under nitrogen and heated for the prescribed time. The product was extracted with NaOH solution and the base extract was acidified and extracted with ether which was dried and evaporated, and the yield of acid was determined by weight. The original organic layer was analyzed by gas chromatography with peak area calibrations using authentic standards.

Reaction of $PhCH_2CO_2T$ (5) with TOH

Ester **5** (100 mg, 0.36 mmol) and 1-hydroxy-2,2,6,6-*N*-tetramethylpiperidine (TOH) (115 mg, 0.72 mmol) in isooctane (5 mL) in an ampoule were degassed for 10 min with dry nitrogen and sealed. The ampoule was heated 2 h in an oil bath at 120 °C. Products identified were $PhCH_2CO_2H$, tetramethylpiperidine (TH), and TEMPO in 40, 45, and 87 % yields respectively. The acid was isolated by extraction with aq. KOH, reacidification with 1 M HCl, and extraction with ether. 2,2,6,6-Tetramethylpiperidine (TH) and TEMPO in the isooctane layer were analyzed by GC.

Kinetics of reaction of $PhCH_2CO_2T$ (5) in hexane with BHT

A solution of **5** and 2,6-di-*tert*-butyl-4 methylphenol (BHT) in hexane (25 mL) was prepared and 100 μL was placed in each of 30 ampoules. The ampoules were sealed and immersed into a temperature regulated oil bath at 120 °C. At regular time intervals ampoules were removed and cooled in ice/water. The extent of conversion was measured by IR from the absorbance of the carbonyl group of **5** and was evaluated using a 1st order fit.

Computational studies. The energies of the reactants and products shown in Scheme 8 obtained at the B3LYP/6-311++G** level are shown in Table 3.

Table 3. Energies (Hartrees) of substrates in Scheme 8

Substrate	*E*	ZPVE	Total
$PhCH_3$	-271.638860	0.127231	-271.511629
$PhCH_2$•	-270.987258	0.113934	-270.873324
HCO_2NH_2	-245.123975	0.049343	-245.074633
HCO_2H	-189.820512	0.033320	-189.787192
$HC(OH)NH_2$•	-245.664198	0.059678	-245.604521

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