JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2003; **16:** 559–563
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.655

Thermolysis of *N*-tetramethylpiperidinyl triphenylacetate: homolytic fragmentation of a TEMPO ester†

Huda Henry-Riyad and Thomas T. Tidwell*

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada

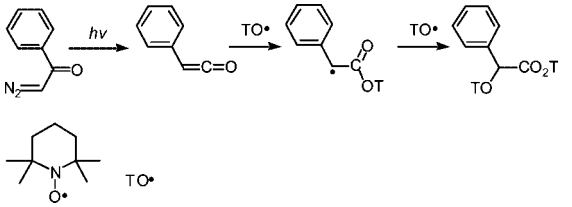
Received 27 October 2002; revised 26 December 2002; accepted 21 March 2003

ABSTRACT: Thermolysis of *N*-tetramethylpiperidinyl triphenylacetate (**7**, Ph_3CCO_2T, T = 2,2,6,6-tetramethylpiperidinyl) in benzene at 146 °C leads to the formation of triphenylmethane (Ph_3CH, 80%), tetramethylpiperidine (TH, 91%), and tetraphenylmethane (Ph_4C, 9%). First-order rate constants for the decomposition at 132.8 and 150.0 °C were 2.20×10^{-6} and $2.88 \times 10^{-5}\,s^{-1}$, respectively. In benzene-d_6 solvent the triphenylmethane was formed as Ph_3CD to the extent of 20%, as determined by ^1H NMR and mass spectrometry. The results are interpreted as showing that Ph_3CCO_2T undergoes thermolysis by concerted two-bond scission with formation of $Ph_3C^{\bullet}$, tetramethylpiperidinyl radicals and CO_2. The formation of Ph_4C occurs by addition of $Ph_3C^{\bullet}$ to benzene, followed by hydrogen atom abstraction from the resulting adduct. Calculations using DFT methods at the B3LYP/6–311++G** level were used to elucidate the bond fission of HCO_2T (**2**), and indicate that cleavage to $HCO_2^{\bullet}$ and $T^{\bullet}$ is favored by 7.8 kcal mol^{-1} relative to cleavage to HC(•)=O and $TO^{\bullet}$, in agreement with the experimental results. Copyright © 2003 John Wiley & Sons, Ltd.
Additional material for this paper is available from the epoc website at http://www.wiley.com/epoc

KEYWORDS: free radicals; TEMPO; triphenylmethyl radical; homolysis

INTRODUCTION

The thermal stability of adducts of tetramethylpiperidinyloxyl (TEMPO, $TO^{\bullet}$) and related aminoxyl radicals plays a prominent role in the trapping of free radicals[1] and in living free radical polymerization.[2] As part of our studies of the reactions of ketenes with aminoxyl radicals,[3] we have generated a number of esters derived from the addition of TEMPO as illustrated for the case of phenylketene, which forms the bis(TEMPO) adduct **1** [Eqn (1)]. The chemistry of such TEMPO adducts is of great interest,[1,3a,b,4,5] but little is known about the reactivity of acyl derivatives, and therefore we have undertaken computational and experimental studies of their properties, beginning with a study of esters RCO_2T (T = *N*-2,2,6,6-tetramethylpiperidinyl).



(1)

*Correspondence to: T. T. Tidwell, Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada.
E-mail: ttidwell@chem.utoronto.ca
†Dedicated to Professor Shinjiro Kobayashi.
Contract/grant sponsor: Natural Sciences and Engineering Research Council of Canada.

The TEMPO ester *t*-$BuCO_2T$ (**2**) was reported to distill at 150 °C without apparent decomposition,[4a] and Studer and co-workers[1b] have reported that $PhCH_2CO_2T$ (**3**) reacted at 150 °C in *tert*-butylbenzene in the presence of O_2 with a rate constant for formation of TEMPO radicals as measured by ESR estimated as $1.1 \times 10^{-9}\,s^{-1}$ at 120 °C for fission of the NO—C bond.[1b] This rate constant was a factor of 10^7 lower than that calculated from a correlation[1d] of $\log k_d$ for dissociation of TEMPO-derived alkoxyamines ROT (R = a hydrocarbon) forming $R^{\bullet}$ and $TO^{\bullet}$ versus the bond dissociation energies for R—H.[1b] The difference was attributed to a much greater strength for the C—O bond in **3** due to interaction with the C=O group, so that the correlation with formation of alkyl radicals would not be expected.[1b] Elucidation of the mechanism involved in this process appeared desirable, and we have therefore undertaken computational studies of model systems and experimental studies of a TEMPO ester expected to generate readily identifiable radicals as a first step in this area.

RESULTS

Computations of the decomposition of the model systems HCO_2NH_2 and HCO_2T with either C—O or N—O cleavage were carried out using DFT methods at the B3LYP/6–311++G**//B3LYP/6–311++G** using

Table 1. Energies (hartree) for dissociation of HCO_2NH_2 and HCO_2T (B3LYP/6–31++G**//B3LYP/6–31++G**)

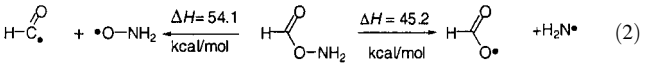
Structure	E	ZPVE[b]	E + ZPVE	S (cal mol^{-1} K^{-1})
HCO_2NH_2	−245.123975	0.049343	−245.074632	68.106
HC(•)O	−113.891332	0.012964	−113.878368	53.585
HCO_2•	−189.142904	0.019575	−189.123329	59.992
H_2NO•	−131.138719	0.025982	−131.112737	58.795
H_2N•	−55.900417	0.018898	−55.881519	46.520
HCO_2T[a]	−597.834837	0.282024	−597.552813	112.678
TO•[a]	−483.855969	0.260681	−483.595288	104.698
T•[a]	−408.617140	0.255041	−408.362099	100.801

[a] T = 2,2,6,6-tetramethylpiperidinyl.
[b] Zero point vibrational energy.

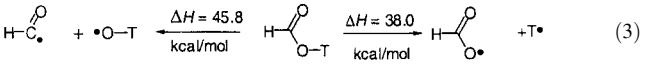
Table 2. Energy changes for dissociation of HCO_2NH_2 and HCO_2T (B3LYP/6–31++G** //B3LYP/6–31++G**), with relative energies in parentheses

Reaction	ΔE (kcal mol^{-1})	ΔE_{298} (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔG (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
$HCO_2NH_2 \rightarrow HC(•)O + H_2NO•$	52.4 (8.6)	53.5 (8.9)	54.1 (8.9)	40.9 (7.2)	44.3
$HCO_2NH_2 \rightarrow HCO_2• + H_2N•$	43.8 (0.0)	44.6 (0.0)	45.2 (0.0)	33.7 (0.0)	38.4
$HCO_2T \rightarrow HC(•)O + TO•$	49.7 (7.4)	45.2 (7.8)	45.8 (7.8)	32.2 (8.5)	45.6
$HCO_2T \rightarrow HCO_2• + T•$	42.3 (0.0)	37.4 (0.0)	38.0 (0.0)	23.7 (0.0)	48.1

Gaussian 98.[6] The calculated energies and entropies are given in Table 1, values of ΔE, ΔE_{298}, ΔH, ΔG and ΔS for these processes are given in Table 2 and the computed values of ΔH are shown in Eqns 2 and 3. For all the comparisons (Table 2) there is a clear prediction that N—O bond cleavage is favored, by amounts ranging from 7.2 to 8.9 kcal mol^{-1} (1 kcal = 4.184 kJ).

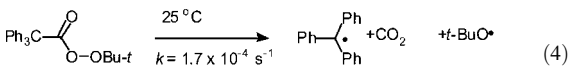


(2)



(3)

Esters of TEMPO bear a structural resemblance to esters RCO_3Bu-*t* of *tert*-butyl peroxide, which are widely used as free radical initiators and have a well-studied chemistry.[7] These species undergo thermal decomposition with cleavage of the O—O bond over a range of temperatures depending on the structure of R, and in the more reactive cases concerted R—C bond cleavage also occurs with formation of R•, *tert*-BuO• and CO_2.[7] One of the most reactive such peroxy esters is *tert*-butyl triphenylperacetate (**4**), which forms triphenylmethyl (**5**), *tert*-butoxy radical (*t*-BuO•) and CO_2 in a concerted process with a rate constant of 1.7×10^{-4} at 25 °C [Eqn (4)].[7a] Because of the evidence of low reactivity of TEMPO esters,[1b,4a] the analogous TEMPO ester derived from triphenylacetic acid was chosen for study.

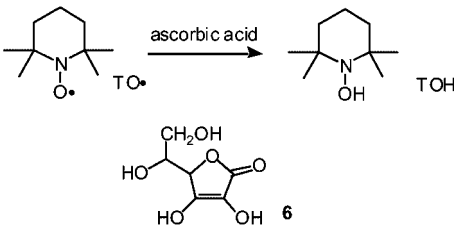


(4)

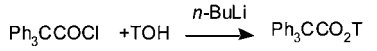
4 **5**

Experimentally, 2,2,6,6-tetramethylpiperidinol (TOH) was prepared by ascorbic acid (**6**) reduction of TEMPO [Eqn (5)].[4b] The tetramethylpiperidinyl ester **7** was prepared by the reaction of the acyl chloride with 2,2,6,6-tetramethylpiperidinol as in Eqn (6).[4]

14



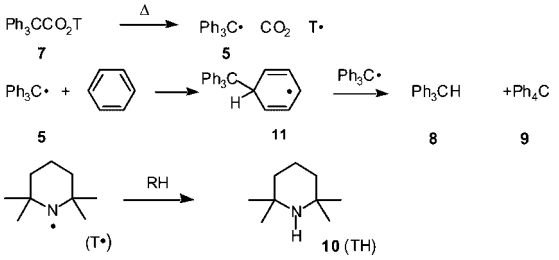
(5)



(6)

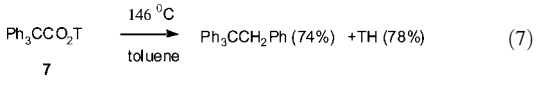
7

The products of thermolysis of **7** in degassed benzene at 146 °C (Scheme 1) were isolated and identified by comparison with authentic materials as triphenylmethane (**8**, 84 ± 4%), tetraphenylmethane (**9**, 8 ± 3%) and tetramethylpiperidine (**10**, TH, 91 ± 3%). Reaction in benzene-d_6 gave **8** (75 ± 4%), containing 20% Ph_3CD as determined by ^{1}H NMR and mass spectrometry, **9** (7 ± 3%) and **10** (93 ± 3%) (Scheme 1). Product yields were determined by vapor-phase chromatography (VPC) calibrated with authentic samples. In samples which had been incompletely degassed, the diphenyl ether $PhOCPh_2CPh_2OPh$ (**12**) of benzpinacol was isolated, and this product could be isolated in high yield when oxygen was added to the reaction mixture prior to thermolysis.



Scheme 1. Thermal decomposition of **7**

The kinetics of reaction of **7** in benzene were measured by an ampoule technique, with IR measurement of the decrease of the carbonyl peak of the ester with time. The data were best fit with a first-order dependence on $[Ph_3CCO_2T]$ and gave rate constants at 132.8 and 150.0 °C of $(2.20 \pm 0.15) \times 10^{-6}$ and $(2.88 \pm 0.80) \times 10^{-5}\,s^{-1}$, respectively. Owing to the experimental difficulties of measuring reaction rates at these temperatures, reliable rate constants over a wider range of temperature could not be obtained, and the data are of insufficient precision to warrant calculation of activation parameters. The products of the reaction of **7** in toluene were determined as 1,1,1,2-tetraphenylethane (74%) and tetramethylpiperidine (78%) [Eqn (7)]. The identification of the isolated 1,1,1,2-tetraphenylethane was confirmed by comparison of the spectral properties with those reported.[8b]



(7)

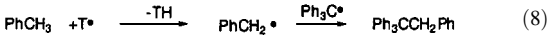
DISCUSSION

The products and first-order kinetic behavior of **7** are consistent with a unimolecular reaction forming CO_2 and the free radicals $Ph_3C^{\cdot}$ and $T^{\cdot}$ (Scheme 1). Preferential reaction of **7** with cleavage of the O—N bond, rather than the C—O bond, is also as predicted by the calculated preference (Table 2) of 6.5–7.8 kcal mol^{-1} for the model system in Eqn (3). The formation of Ph_3CH (**8**) and tetramethylpiperidine (TH, **10**) would occur by hydrogen abstraction reactions, while tetraphenylmethane (**9**, Ph_4C) could be formed by addition of triphenylmethyl radical to benzene forming the radical **11**, which loses a hydrogen atom to $Ph_3C^{\cdot}$ or to tetramethylpiperidinyl radical ($T^{\cdot}$). The experiment in benzene-d_6 forming 20% Ph_3CD confirms the role of intermediate **11**, but the incomplete deuteration found and the high yield of TH (**10**) show that there are other sources of H atoms available, possibly the piperidine rings or the head-to-tail dimer of $Ph_3C^{\cdot}$.

The rate constant of **7** at 150 °C of $2.88 \times 10^{-5}\,s^{-1}$ exceeds that of $1.1 \times 10^{-9}\,s^{-1}$ reported[1b] for $PhCH_2CO_2T$ (**3**) by a factor of 2.6×10^4, and this large rate enhancement is strong evidence that the reaction of **7** occurs with concerted breaking of the N—O and Ph_3C—C bonds leading to the persistent radical $Ph_3C^{\cdot}$. This rate enhancement may be compared with that of 2.7×10^3 at 25 °C for the perester Ph_3CCO_3Bu-*t* compared with $PhCH_2CO_3Bu$-*t*, both of which are interpreted as reacting with concerted cleavage of the C—CO and O—O bonds.[7]

The rate constant of **7** at 132 °C of $2.20 \times 10^{-6}\,s^{-1}$ may be compared with the extrapolated rate constant of $10^2\,s^{-1}$ for Ph_3CCO_3Bu-*t*, indicating that **7** is less reactive by a factor of 10^8. This large difference shows the influence of the greater bond dissociation energy for an N—O compared with an O—O bond.

The reaction of **7** in toluene occurs by the same first step as in Scheme 1, and then the tetramethylpiperidinyl radical abstracts hydrogen from toluene forming tetramethylpiperidine and a benzyl radical. Combination of the triphenylmethyl and benzyl radicals forms tetraphenylethane [Eqn (8)].



(8)

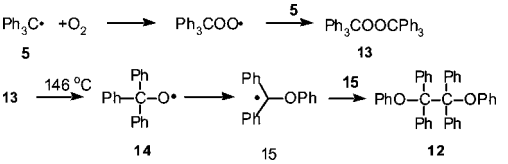
The ether **12** in the presence of O_2 results from the reaction of $Ph_3C^{\cdot}$ with O_2 followed by formation of the peroxide **13** and Wieland rearrangement[8a] by cleavage of the peroxidic O—O bond with formation of oxyl radicals **14** which undergo phenyl migration from C to O and then combination (Scheme 2). This process is known to occur at these temperatures.[8a] Authentic samples of **12** and **13** were prepared to confirm the identifications.

As noted above, the reaction of $PhCH_2CO_2T$ (**3**) at 150 °C occurs with the formation of TEMPO,[1b] but this experiment was carried out in the presence of O_2, which could react with initially formed tetramethylpiperidinyl radicals $T^{\cdot}$ forming TEMPO. This reactivity of **3** and those of related esters of TEMPOH are under further investigation.

In summary, DFT calculations predict that homolysis of *N*-formyloxy-2,2,6,6-tetramethylpiperidine (HCO_2T) favors cleavage of the N—O bond forming $HCO_2^{\cdot}$ and $T^{\cdot}$. In agreement with this prediction, experimental studies of Ph_3CCO_2T (**7**) show that this reacts by concerted thermal decomposition at 132–150 °C forming $Ph_3C^{\cdot}$, CO_2 and $T^{\cdot}$, with a rate constant at 150 °C that is 2.6×10^4 times greater than that of $PhCH_2CO_2T$ (**3**).

COMPUTATIONAL STUDIES

Computations were carried out at the B3LYP/6–311++G**//B3LYP/6–311++G** level using Gaussian



Scheme 2. Reaction of triphenylmethyl oxygen

98[6] with a computer cluster from Velocet Communications (Toronto, Canada). The calculated energies and entropies are given in Table 1 and the energy changes in Table 2.

EXPERIMENTAL

Gas chromatography. GC analysis was carried out using a flame ionization detector and a Simplicity 5 column (poly-5% diphenyl-95% dimethylsiloxane). Authentic samples were used to calibrate the response for quantitative product analysis.

Preparation of 1-hydroxy-2,2,6,6-tetramethylpiperidine (TOH).[4] A suspension of TEMPO (1 g, 6.4 mmol) in a solution of sodium ascorbate (2.1 g, 10.6 mmol) prepared from 1.87 g of ascorbic acid and 0.42 g of NaOH in water (18 ml) was stirred vigorously until completely decolorized with the appearance of a white precipitate (ca 5 min). The resulting suspension was extracted with diethyl ether and the ether extracts were washed with water and brine, dried over anhydrous sodium sulfate and evaporated under reduced pressure to provide TOH (0.94 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.20 (s, 12), 1.55 (s, 6). ^{13}C NMR (100 MHz, $CDCl_3$), δ 12.1, 34.5, 53.7. IR (pentane), 3590 cm^{-1}. EIMS, *m/z* 157, 156, 142, 109, 83, 69, 55. ^{1}H NMR (500 MHz, $CDCl_3$, $-60\,^\circ$C), δ 1.10 (s, 6), 1.18 (s, 6), 1.40 (m, 4), 1.56 (m, 2), 2.26 (s, 1). ^{13}C NMR (500 MHz, $CDCl_3$, $-60\,^\circ$C), δ 16.8, 18.9, 32.2, 39.1, 58.7.

*N-triphenylacetoxy-2,2,6,6-tetramethylpiperidine (**7**).* Triphenylacetyl chloride (520 mg, 1.7 mmol) prepared from the reaction of triphenylacetic acid (0.5 g, 1.7 mmol) and oxalyl chloride (0.36 ml, 4.25 mmol) with 2 drops of DMF was added to a stirred solution of 1-hydroxy-2,2,6,6-tetramethylpiperidine (270 mg, 1.7 mmol) and *n*-BuLi (1 ml, 1.6 mmol) in 50 ml of CH_2Cl_2. The reaction mixture was stirred for 20 min and 40 ml of 10% HCl were added. The organic layer was washed with 3×20 ml of brine, dried over $MgSO_4$, and concentrated. Column chromatography (silica gel with CH_2Cl_2) gave **7** as white crystals, m.p. 139–142 °C (470 mg, 1.2 mmol, 65%). ^{1}H NMR (100 MHz, $CDCl_3$), δ 0.86 (s, 6, 2CH_3), 0.98 (s, 6, 2CH_3), 1.1–1.7 (m, 6, 3 CH_2), 7.23–7.34 (m, 15, 3Ph). ^{13}C NMR (100 MHz, $CDCl_3$), δ 17.4, 21.4, 32.3, 39.9, 60.8, 65.7, 127.0, 127.7, 130.8, 142.7. IR ($CDCl_3$), 1749 cm^{-1}; (toluene), 1754 cm^{-1}. EIMS, *m/z* 427 (M^+), 271 ($M^+ - TO$), 243 (PhC^+), 165, 97, 82, 69, 56. HREIMS, *m/z* calc. for $C_{29}H_{34}NO_2$, 428.25899; found, 428.25896.

*Products of N-triphenylacetoxy-2,2,6,6-tetramethylpiperidine (**7**) thermolysis in benzene.* A solution of **7** (20 mg, 0.046 mmol) in 1 ml of benzene in a flame-dried ampoule was degassed by either 15 min of bubbling in N_2 or by four freeze–thaw cycles. Duplicate runs were carried out with each degassing method, with the same results. The ampoules were heated for 26 h (for C_6H_6) or 48 h (for C_6D_6) and the products analyzed by gas chromatography. The runs in C_6H_6 gave Ph_3CH ($82 \pm 3\%$), tetramethylpiperidine ($92 \pm 3\%$) and Ph_4C ($9 \pm 3\%$), and runs in C_6D_6 gave $Ph_3CH(D)$ ($76 \pm 4\%$, containing 20% D by MS), tetramethylpiperidine ($93 \pm 3\%$) and Ph_4C ($7 \pm 3\%$). The composition of Ph_3CD was confirmed by HREIMS: m/z calc. for $C_{13}H_{15}D$, 245.13095; found, 245.13148.

*Products of N-triphenylacetoxy-2,2,6,6-tetramethylpiperidine (**7**) thermolysis in toluene.* A solution of **7** (20 mg, 0.046 mmol) in 1 ml of toluene in a flame-dried ampoule was degassed by four freeze–thaw cycles and heated for 40 h at 146 °C. The products were analyzed by gas chromatography as tetramethylpiperidine ($78 \pm 4\%$) and Ph_3CCH_2Ph. The latter product was isolated in 74% yield and identified by comparison of its spectral properties with those reported.[8b] ^{1}H NMR (400 MHz, $CDCl_3$), δ 3.96 (s, 2, CH_2), 6.64 (d, 2, $J = 7.1$ Hz, *o*-H), 7.0–7.1 (m, 4, *m*- and *p*-H), 7.16–7.36 (m, 15, 3Ph). ^{13}C NMR (100 MHz, $CDCl_3$), δ 46.5, 58.7, 58.7, 126.1, 127.5, 127.8, 128.2, 130.0, 131.4, 142.7, 146.8. EIMS, m/z 333 ($M^+ - H$), 243 (Ph_3C^+), 165, 91. HREIMS, m/z calc. for $C_{26}H_{21}$, 333.16438; found, 333.16433.

*Kinetics of N-triphenylacetoxy-2,2,6,6-tetramethylpiperidine (**7**) thermolysis.* Aliquots (0.2 ml) of a solution of **7** (50 mg in 5 ml of benzene) were sealed in 20 ampoules, which were divided into two batches that were heated in an oil-bath. Ampoules were withdrawn at intervals and the residual substrate was determined from the change in the integrated IR signal at 1754 cm^{-1}, which was fit to first-order kinetics. Duplicate runs gave first-order rate constants of $(2.20 \pm 0.20) \times 10^{-6}$ s^{-1} at 132.8 °C and $(2.88 \pm 0.80) \times 10^{-5}$ s^{-1} at 150.0 °C.

Tetraphenylmethane. Phenylazotriphenylmethane (0.70 g, 2.0 mmol) in 10 ml of benzene was refluxed for 2 h, giving a dark red solution which changed to yellow on cooling. The solvent was evaporated and the residue chromatographed (silica gel, CH_2Cl_2) to give tetraphenylmethane (0.11 g, 10%).[8c] ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.28 (s, 20, 4Ph). ^{13}C NMR (400 MHz, $CDCl_3$), δ 127.5, 128.2, 128.5, 130.3, 132.7, 147.1. EIMS, m/z 320 (M^+), 243 (Ph_3C^+), 165, 105. HREIMS, m/z calc. for $C_{25}H_{20}$, 320.15595; found, 320.15650.

Trityl peroxide.[8a,d–f] Zinc dust (0.5 g, 7.5 mmol) and triphenylmethyl chloride (1 g, 3.6 mmol) in 20 ml of cyclohexane were stirred for 30 min open to the atmosphere. Filtration gave solid trityl peroxide (71%), which was recrystallized from toluene. ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.24–7.32 (m, 30, 6 Ph). ^{13}C NMR (100 MHz, $CDCl_3$), δ 128.2, 128.3, 128.4, 130.2, 145.7. EIMS, m/z 259 (Ph_3CO^+, 100), 243 (Ph_3C^+, 90), 165, 105, 77; lit.[8e] 259 (100), 243 (73). Upon heating melting begins at 110 °C, and ^{1}H NMR shows partial rearrangement at this point, which is complete on heating to 190 °C.

Thermolysis of trityl peroxide: formation of 1,2-diphenoxy-1,1,2,2-tetraphenylethane.[8a] Trityl peroxide (100 mg, 0.019 mmol) in 5 ml of benzene was degassed under nitrogen for 15 min and heated for 6 h at 150 °C. The solvent was evaporated and the product **12** identified by the spectral properties. ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.21–7.33 (m, 20, 4 Ph), 7.49–7.54 (m, 4, *m*-H), 7.60–7.62 (m 2, *p*-H), 7.82 (d, 4, $J = 8.5$ Hz, *o*-H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 127.4, 127.8, 127.9, 128.1, 128.4, 129.8, 130.2, 132.5, 145.3. EIMS, m/z 260 [$Ph_2C(OPh)H^+$, 46], 243 (Ph_3C^+, 44), 183, 165, 154, 105, 77.

Supplementary material

Rate plots for **7** and a table of computed thermodynamic properties are available at the epoc website at http://www.wiley.com/epoc.

Acknowledgement

Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

REFERENCES

1. (a) Studer A. *Angew Chem., Int. Ed. Engl.* 2000; **39**: 1108–1111; (b) Marque S, Fischer H, Baier E, Studer A. *J. Org. Chem.* 2001; **66**: 1146–1156; (c) McCarroll AJ, Walton JC. *J. Chem. Soc., Perkin Trans. 2* 2000; 2399–2409; (d) Marque S, Le Mercier C, Tordo P, Fischer H. *Macromolecules* 2000; **33**: 4403–4410; (e) Ciriano MV, Korth H-G, van Scheppingen WB, Mulder P. *J. Am. Chem. Soc*. 1999; **121**: 6375–6381; (f) Sobek J, Martschke R, Fischer H. *J. Am. Chem. Soc*. 2001; **123**: 2849–2857; (g) Kothe T, Marque S, Martschke R, Popov M, Fischer H. *J. Chem. Soc., Perkin Trans. 2* 1998; 1553–1559; (h) Babiarz JE, Cunkle GT, DeBellis AD, Eveland D, Pastor SD, Shum SP. *J. Org. Chem.* 2002; **67**: 6831–6834.
2. (a) Georges MK, Veregin RPN, Kazmaier PM, Hamer GK. *Macromolecules* 1993; **26**: 2987–2988; (b) Hawker CJ. *Acc. Chem. Res.* 1997; **30**: 373–382; (c) Nakamura T, Busfield WK, Jenkins ID, Rizzardo E, Thang SH, Suyama S. *J. Am. Chem. Soc*. 1997; **119**: 10987–10991; (d) Patten TE, Matyjaszewski K. *Acc. Chem. Res*. 1999; **32**: 895–903.
3. (a) Allen AD, Fenwick MH, Henry-Riyad H, Tidwell TT. *J. Org. Chem.* 2001; **66**: 5759–5765; (b) Huang W, Henry-Riyad H, Tidwell TT. *J. Am. Chem. Soc*. 1999; **121**: 3939–3943; (c) Allen AD, Cheng B, Fenwick MH, Huang W, Missiha S, Tahmassebi D, Tidwell TT. *Org. Lett*. 1999; **1**: 693–696; (d) Allen AD, Cheng B, Fenwick MH, Givehchi B, Henry-Riyad H, Nikolaev VA, Shikova EA, Tahmassebi D, Tidwell TT, Wang S. *J. Org. Chem.* 2001; **66**: 2611–2617; (e) Carter J, Fenwick MH, Huang W, Popik VV, Tidwell TT. *Can. J. Chem*. 1999; **77**: 806–809; (f) Allen AD, Porter J, Tahmassebi D, Tidwell TT. *J. Org. Chem.* 2001; **66**: 7420–7426; (g) Fenwick MH, Tidwell TT. *Eur. J. Org. Chem.* 2001; 3415–3419; (h) Allen AD, Rangwalla H, Saidi K, Tidwell TT, Wang J. *Russ. Chem. Bull.* 2001; 2130–2133; (i) Sung K, Tidwell TT. *J. Org. Chem*. 1998; **63**: 9690–9697; (j) Allen AD, Fenwick MH, Jabri A, Rangwala H, Saidi K, Tidwell TT. *Org. Lett*. 2001; **3**: 4095–4098; (k) Saidi K, Tidwell TT. *ARKIVOC* 2001; **2**: 100–107.
4. (a) Anderson JE, Corrie JET. *J. Chem. Soc., Perkin Trans. 2* 1992; 1027–1031; (b) Anderson JE, Casarini DJ, Corrie JET, Lunazzi L. *Chem. Soc., Perkin Trans. 2* 1993; 1299–1304.
5. (a) Nakamura T, Busfield WK, Jenkins ID, Rizzardo E, Thang SH, Suyama S. *J. Org. Chem*. 2000; **65**: 16–23; (b) Benoit D, Chaplinski V, Braslau R, Hawker CJ. *J. Am. Chem. Soc*. 1999; **121**: 3904–3920; (c) Braslau R, Burrill LC, II, Siano M, Naik N, Howden RK, Mahal LK. *Macromolecules* 1997; **30**: 6445–6550; (d) Kothe T, Marque S, Martschke R, Popov M, Fischer H. *J. Chem. Soc., Perkin Trans. 2* 1998; 1553–1559; (e) Jahn U. *J. Org. Chem*. 1998; **63**: 7130–7131.
6. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Jr., Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. Gaussian 98, Revision A.9. Gaussian: Pittsburgh, PA, 1998.
7. (a) Lorand JP, Bartlett PD. *J. Am. Chem. Soc*. 1966; **88**: 3294–3302; (B) Singer LA. In *Organic Peroxides*, vol. **1**, Swern D (ed). Wiley: New York, 1970; 265–312.
8. (a) Wieland H. *Chem. Ber.* 1911; **44**: 2550–2556; (b) Watkins MI, Olah GA. *J. Am. Chem. Soc*. 1981; **103**: 6566–6574; (c) Kryger RG, Lorand JP, Stevens NR, Herron NR. *J. Am. Chem. Soc.* 1977; **99**: 7589–7600; (d) Branchaud BP. *J. Org. Chem.* 1983; **48**: 3538–3544; reported ^{1}H NMR 7.17 (pseudo singlet) and m.p. 189–195 °C;[8g] (e) Takeuchi H, Nagai T, Tokura N. *Tetrahedron* 1969, **25**: 2987–2998; reported ^{1}H NMR 6.7–6.9, m.p. 183 °C;[8g] (f) Cook AF, Moffatt JG. *J. Am. Chem. Soc*. 1967; **89**: 2697–2705; (g) The mp in ref 8d and 8e correspond to that of the product 12 of Wieland rearrangement, and not to that of trityl peroxide (13).