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Thermolysis of a Tertiary Alkoxyamine. Recombination and Disproportionation of α-Phenethyl/Diethyl Nitroxyl Radical Pairs

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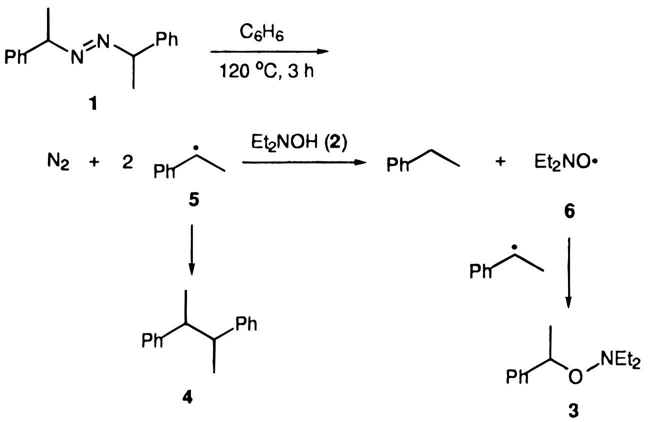
Alkoxyamine **3** undergoes thermolysis only on heating to over 150 °C, $\Delta H^{\ddagger} = 34.3 \pm 1.6$ kcal/mol and $\Delta S^{\ddagger} = 0.8 \pm 3.7$ eu. The initially formed nitroxyl (**6**) and α-phenethyl radicals (**5**) mainly disproportionate to styrene plus diethylhydroxylamine (**2**) but they also recombine to starting material and undergo a new reaction, disproportionation to ethylbenzene plus nitrone (**12**). The latter reacts with the styrene product to yield oxazolidines **8** and **9**. The competition between attack of **5**, generated from azo-α-phenylethane (**1**), on **2** versus styrene allowed us to calculate a rate constant at 120 °C of 5×10^3 M^{-1} s^{-1} for $H^{\bullet}$ transfer from diethylhydroxylamine to **5**.

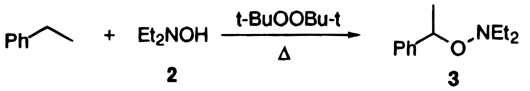
Diethylhydroxylamine (DEHA) has found extensive application as an inhibitor of vinyl polymerization.[1] A likely product of such inhibition is the tertiary alkoxyamine (TAA) arising from recombination of propagating chains with diethylnitroxyl radicals. When the nitroxyl moiety is hindered, the corresponding TAA's serve as initiators of living free radical polymerization, an area that has received much recent attention.[2−7] Depending on the stability of the incipient radicals and on the degree of steric crowding, TAA's exhibit half-lives ranging from 18 min at 40 °C to >1000 min at 80 °C.[4] Presently, we describe the chemistry of α-phenethyl/diethyl nitroxyl radical pairs from a less crowded and therefore more stable TAA.

Preparation of *N*-(1-phenylethoxy)diethylamine (3)

Thermolysis of 0.016 M azoalkane **1**[8] with 0.045 M diethylhydroxylamine (**2**) in benzene led to TAA **3**. The ratio of ethylbenzene to dimers **4** was 0.23 versus the 0.018 ratio found in the absence of **2**, showing that **2** scavenges α-phenethyl radicals **5**. The resulting nitroxyl radical **6** reacts with the second molecule of **5** to afford **3**. Since **4** arises partly by cage recombination, this product cannot be completely suppressed.



Most TAA's reported previously were made by scavenging alkyl radicals with the isolable nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (Tempo).[2−4,6,9−11] A sufficient amount of **3** to study its chemistry was obtained by refluxing ethylbenzene (bp 136 °C) with di-*tert*-butyl peroxide and **2**. Although the yield was only 2.6% and column chromatography was required for purification, this unlikely looking synthesis of **3** proceeds in one step from inexpensive starting materials. GC monitoring of the reaction showed that the concentration of **3** leveled off and then declined at long reflux times, suggesting that this TAA ultimately dissociates. Indeed, attempts to isolate **3** by preparative GC led only to decomposition on the column. The NMR spectrum of **3** was in accord with its structure, but both the methyl and methylene signals of the ethyl group were broadened by slow inversion through nitrogen.[12]



Thermolysis of 3

A sample of 0.061 M **3** in C_6D_6 was degassed and sealed in an NMR tube. Thermolysis at 170.0 °C monitored by NMR led to a first-order disappearance rate constant $k = (1.62 \pm 0.06) \times 10^{-4}$ s^{-1} (half-life 71 min). A series of kinetic runs using five sealed tubes each, analyzed by GC, was then carried out at 155.1, 170.0, and 185.3 °C, giving $k = (4.24 \pm 0.05) \times 10^{-5}$, $(1.52 \pm 0.02) \times 10^{-4}$,

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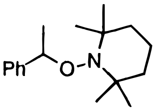
Table 1. Thermolysis Products of 3[a]

product	relative area (GC)[b]	relative yield (NMR)[c]
styrene	100	100
ethylbenzene	14.8	[d]
oxazolidines **8** and **9**	42	34
diphenylbutane **10**	4.9	8.6[e]
diphenylbutene **11**	30	12.4
diethylhydroxylamine **2**	[f]	64

[a] 170 °C in C_6D_6 for 15 h. [b] Relative GC peak areas (FID detector). [c] By integrating a characteristic peak of each product. [d] Not determined on account of excessive peak overlap. [e] This figure is a maximum because other peaks obscure **10**. [f] **2** cannot be seen by GC.

and $(6.44 \pm 0.08) \times 10^{-4}$ s^{-1}, respectively. The derived activation parameters are $\Delta H^{\ddagger} = 34.3 \pm 1.6$ kcal/mol and $\Delta S^{\ddagger} = 0.8 \pm 3.7$ eu. We may compare our $\Delta H^{\ddagger}$ with a theoretical[7] and two experimental values[2,6] for **7**, namely



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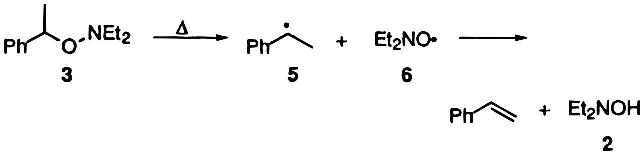
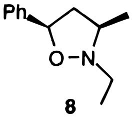
33.7, 27.6, and 31.1 kcal/mol, respectively. Neither of the experimental studies provided absolute rate data, but from the graph in ref 2, we calculate $\Delta G^{\ddagger}(160\ °C) = 32.4$ kcal/mol, which is 1.6 kcal/mol below our $\Delta G^{\ddagger}(160\ °C)$. This difference is attributed to ground state strain[4,10] in **7**, because the radicals formed from both TAA's are of essentially the same thermodynamic stability.[13] A control experiment was run to test whether the decomposition of **3** was induced by α-phenethyl radicals. On heating **3** with **1** in C_6D_6 in a degassed, sealed NMR tube at 120 °C for 3 h, the intensity of the signals due to **3** remained unchanged. NMR and GC analysis of **3** thermolyzed to completion revealed that the major products were styrene and **2**, formed by the usual homolysis–disproportionation pathway of TAA's[10,14] (cf. Table 1). The α-phenethyl radical dimers **4** that were almost the exclusive product from **1** were absent. Of greater interest were the minor products ethylbenzene and **8**–**11**. The latter were isolated by preparative TLC and their structures determined by MS, NMR, and authentic synthesis. Oxidation[15] of diethylamine afforded nitrone **12**, which was heated with styrene to yield diastereomeric oxazolidines **8** and **9**.[16] Comparison of their NMR spectra with those of similar oxazolidines[17] supported the assigned structures. 1,3-Diphenyl-1-butene **11** was prepared from α-phenylpropanal by a Wittig reaction with benzyltriphenylphosphonium chloride. The product was a 3:2 *E*:*Z* mixture that afforded **10** on catalytic hydrogenation. Thermolysis of **3** gave only **11E**, an authentic sample of which was isolated by flash column chromatography of the Wittig product.





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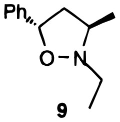

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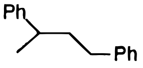

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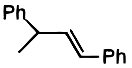

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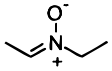

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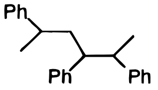
Table 2. Products from Thermolysis of 1, 2, and Styrene[a]

product	retention time, min[b]	relative area (GC)
ethylbenzene	7.15	8.6
styrene	7.61	200
TAA **3**	14.59	33.4
oxazolidines **8** and **9**	16.97, 17.18	12.0
diphenylbutanes **4**	19.29	100
diphenylbutane **10**	20.03	0.45
diphenylbutene **11**	20.25	1.30
unknown	23.26	1.50
trimers **13**	26.48, 26.59, 27.28, 28.47	5.50
trimers **14a,b**	28.67, 29.30	0.41
unknown, MW 312	29.74	0.49

[a] 120 °C in C_6H_6 for 3 h. [b] DB-5 column; see Experimental Section.

To aid in deducing the origin of ethylbenzene, **8**, and **9**, eight tubes containing **3** in C_6H_6 were degassed, sealed, and placed into a 170 °C oil bath. The tubes were removed at intervals, opened, and analyzed by GC. Whereas the ethylbenzene evolved linearly from the beginning, **8** and **9** showed a gradually increasing slope. These results suggest that ethylbenzene is a primary product but **8** and **9** arise by a secondary process, which we propose is 1,3-dipolar cycloaddition of **12** with styrene. The same reaction is possible during the synthesis of **3** from the 120 °C thermolysis of **1** plus **2**, but we did not observe the oxazolidines in this case. Because styrene was a very minor product in the reaction of **1** with **2** and was therefore hardly available to trap **12**, we added 1 equiv of styrene at the outset. A benzene solution of 0.02 M each in **1** and **2**, and styrene was heated at 120° for 3 h, after which **8** and **9** were easily detected by GC (cf. Table 2).

This experiment with **1**, **2**, and styrene revealed additional GC peaks at longer retention time that proved significant in another context. Thus the presence of **10** and **11** immediately showed that α-phenethyl radicals attack styrene in this system. Another set of four GC peaks of nearly the same size and retention time (~27 min) exhibited identical EI mass spectra (MW 314). These peaks were assigned structure **13**, whose three asymmetric centers lead to four diastereomers.[18,19] Al-



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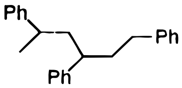

14 a,b

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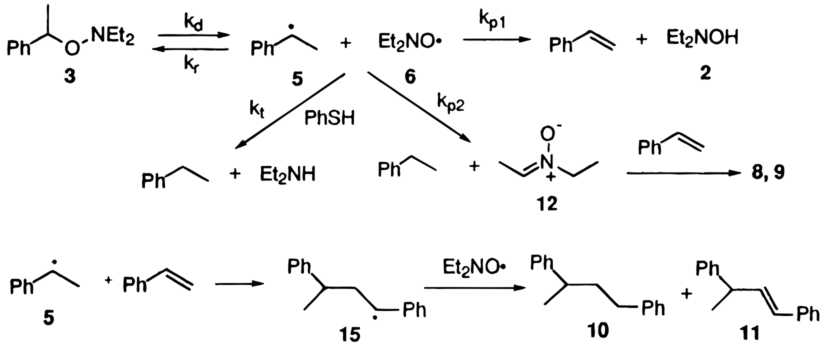
[18] The four diastereomeric styrene trimers have been synthesized previously. Schaltegger, H.; Moser, K.; Hunkeler, W. S.; Wenger, T. *Chimia* **1967**, *21*, 91.

[19] A radical consisting of an initiator fragment and two styrenes has been trapped by 1,1,3,3-tetramethylisoindolinyl-2-oxyl, see: Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909.

Scheme 1. Reactions of Free Radicals from 3



ternative structure **14** would give only two diastereomers, and indeed, we observed two small, equal sized GC peaks of longer retention time that were tentatively assigned structure **14a,b**. Their mass spectra were similar to that of **13** but they displayed a much larger $m/e = 91$ peak, consistent with a benzyl group.[20]

Dissociation processes in solution, particularly of TAA's,[10] are normally accompanied by a significant amount of recombination to starting material. To assess this possibility, a 0.064 M C_6D_6 solution of **3** was heated at 170 °C with 0.123 M PhSH, an excellent scavenger for nitroxyl[21] and alkyl[22] radicals. NMR monitoring of the kinetics gave a first-order rate constant of $(4.87 \pm 0.12) \times 10^{-4}$ s^{-1}, about 3 times faster than **3** alone. Raising the PhSH concentration to 1.42 M gave only a slightly faster rate constant, $(5.54 \pm 0.08) \times 10^{-4}$ s^{-1}. The rate acceleration and the nature of the major products (ethylbenzene, Et_2NH, and PhSSPh but not **8** nor **9** and hardly any styrene) suggest that PhSH diverted radicals **5** and **6** away from reforming **3** by simply reducing them. The reaction of nitroxyl radicals with PhSH is already known to afford the amine plus PhSSPh.[10,21]

Li *et al.*[9] reported that heating neat TAA **7** to 57 °C in an ESR spectrometer gave rise to the characteristic triplet of Tempo. We gradually heated a degassed, sealed 0.026 M hexadecane solution of **3** to 200 °C and finally observed a weak ESR signal that was readily assigned to **6**.[23]

Discussion

Thermolysis of **3** yields α-phenethyl/nitroxyl radical pairs that react by recombination and disproportionation in two directions, k_{p1} and k_{p2} (cf. Scheme 1). As judged from the high yield of styrene and **2**, k_{p1} is the dominant pathway; however, k_{p2} represents a new reaction, as will be discussed shortly. Despite the fact that **5** is consumed by reaction with **6** and that styrene cycloadds to **12**, **5** manages to find styrene and begin polymerization. However, this process is cut short as radical **15** reacts with $Et_2NO^{\bullet}$ in the same manner as **5** did, namely by disproportionation to afford **10** and **11**. Only the *E* isomer of **11** is formed, most likely because the 1,2 bond of **15** exists mainly in the *s-trans* conformation.

Although nitrone **12** is not observed on GC, its well-behaved 1,3-dipolar cycloaddition products with styrene (**8** and **9**) implicate **12** as a reaction intermediate.[16] These oxazolidines grew in with an increasing slope, consistent with their being secondary products. We propose that the nitrone arises from cross disproportionation of **5** and **6**, with the nitroxyl radical serving as the $H^{\bullet}$ donor (pathway k_{p2} of Scheme 1). Although we are unaware of any such reaction in previously studied TAA's (*e.g.* **7**), these compounds were derived from nitroxyls like Tempo, which possess no hydrogens α to N. The question then arises whether all of the **2** and **12** formed during thermolysis of **3** comes from cross disproportionation or whether there is any contribution from self-disproportionation of $Et_2NO^{\bullet}$. We find no dimer **4** in this reaction, even though recombination of α-phenethyl radicals **5** is vastly faster[24] than self-reaction of $Et_2NO^{\bullet}$ ($k = 3.2 \times 10^4$ M^{-1} s^{-1} at 170 °C).[23] Since each molecule of **5** is accompanied by one of **6**, the fact that **5** does not dimerize indicates that **6** does not disproportionate.

Ethylbenzene is a minor thermolysis product of **3** that could arise by disproportionation of **5** with **6** (Scheme 1, k_{p2}) or by a secondary reaction in which α-phenethyl radicals abstract $H^{\bullet}$ from **2**, which builds up as the reaction proceeds. The formation of **12** coupled with the nonzero initial slope of our plot of ethylbenzene versus time indicates that most of the ethylbenzene arose via k_{p2}. However, we cannot rule out some contribution from the secondary reaction of **5** with **2**. In the case of **7**, which has no hydrogens α to nitrogen, only the secondary reaction is possible, consistent with the apparent zero initial slope of the two point ethylbenzene versus time plot.[2]

The weakness of the ESR signal due to **6** when **3** was heated over 200 °C shows that the concentration of **6** is never very high. In contrast, mild heating of **7** led to a large Tempo ESR signal,[9] surely because Tempo is more hindered and less reactive than **6**. No dimers **4** are found in the thermolysis of **3**, but they were a major product of **7**. Again, the much greater stability of Tempo than **6** accounts for this product difference.

An important fate of radicals **5** and **6** is actually recombination, as demonstrated by the 3-fold rate acceleration when PhSH is included in the thermolysis of **3**. According to Scheme 1, the disappearance rate of **3** without PhSH is $r_o = k_d f k_p/(k_p + k_r)$ where f is the fraction of cage escape and k_p is the sum of k_{p1} and k_{p2}. When PhSH is present, the rate is $r = k_d f(k_p + k_t[\mathrm{PhSH}])/(k_r + k_p + k_t[\mathrm{PhSH}])$. At very high PhSH concentration, we may therefore write $r_{\infty}/r_o = 1 + k_r/k_p$. If we assume that the PhSH concentration employed (0.123 M) was sufficient to scavenge all free (noncage) radicals, then the

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[20] Unlike diastereomers **13**, the mass spectra of **14a** and **14b** were not identical; hence, their structure assignment is only tentative.

[21] Murayama, K.; Yoshioka, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1942.

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observation that $r_\infty = 3r_o$ implies that the recombination rate k_r of free **5** and **6** pairs is twice their disproportionation rate k_p. A much higher PhSH concentration (1.42 M) caused only a 14% additional rate increase, which we attribute to the known effect of solvent polarity on TAA thermolysis rates[10] and which therefore indicates that 0.123 M PhSH was a completely effective scavenger. $H^\bullet$ transfer from PhSH to nitroxyl radicals is facile,[21,25] but no rate constant seems to be available. The rate constant for **5** with PhSH is at least 10^6 M^{-1} s^{-1} at the reaction temperature of 120 °C,[26] a high enough value that all free radicals should be scavenged at the PhSH concentrations employed.

The formation of **10**, **11**, **13**, and **14** from **1**, **2**, and styrene shows that styrene suffers attack by **5** despite the presence of the hydrogen donor **2**, and a quantitative treatment allows calculation of an approximate $H^\bullet$ transfer rate. The rate constant for styrene polymerization (k_{prop}) at 120 °C is 2.2×10^3 M^{-1} s^{-1}, based on our own least squares fit of 39 data points.[27] In view of the poor correlation coefficient (0.886) and the extrapolation outside the experimental temperature range, k_{prop} is more realistically expressed as $(2 \pm 1) \times 10^3$ M^{-1} s^{-1}. Using this rate as a radical clock, we derive the equation $k_{H^\bullet}/k_{prop}$ = ([styrene]/[**2**])(moles of PhEt/(moles of **10** + **11** + **13** + **14** + unknowns)). It follows from the product composition (Table 2)[28] and the initial concentration of styrene and **2** that the hydrogen transfer rate from **2** to **5** is 5×10^3 M^{-1} s^{-1} at 120 °C. From the bond dissociation energy of ethylbenzene[29] and Tempo[13] (85.4 and 71.8 kcal/mol, respectively), we calculate that this slow hydrogen transfer is exothermic by 13.6 kcal/mol. Previous literature on $H^\bullet$ abstraction rates from hydroxylamines is confined to the observations that *t*-$Bu^\bullet$ abstracts $H^\bullet$ from **2** 1.2 times faster than from isoprene[30] and that the $H^\bullet$ transfer rate from **2** to ethyl radicals in the gas phase at 25 °C is 7.7×10^5 M^{-1} s^{-1}.[31] Our rate constant is comparable in magnitude to primary alkyl abstracting $H^\bullet$ from dodecane, $k = 3.5 \times 10^3$ M^{-1} s^{-1} at 100 °C.[32]

The thermolysis of **3** at 170 °C, where disproportionation is the major net reaction, contrasts with the generation of **3** from **1** at 120 °C, where only a little styrene is observed. The fact that **3** is a product of **1** + **2** shows that α-phenethyl and **6** are present at the same time, yet they hardly disproportionate. Although this discrepancy might be attributed to the lower temperature of the reaction involving **1**, disproportionation to recombination ratios do not vary that strongly with temperature.[14,33] A partial explantion for this change in products is that recombination is always the main fate of **5** and **6** pairs but at 170 °C, recombination is invisible and disproportionation, an irreversible process, is the only observed reaction.

In summary, alkoxyamine **3** is more stable thermally than analogs derived from stable nitroxyl radicals.[2,4,6,7,10] On heating to 170 °C, it disproportionates mainly to styrene and diethylhydroxylamine **2** but, in a new reaction, it also yields ethylbenzene and nitrone **12**. The latter then undergoes 1,3-dipolar cycloaddition to the formed styrene to afford diastereomeric oxazolidines **8** and **9**. Some of the styrene suffers attack by α-phenethyl radicals, yielding dimers **10** and **11**. The reaction of diethylhydroxylamine with α-phenethyl radical is slow ($k = 5 \times 10^3$ M^{-1} s^{-1}) relative to many other hydrogen transfers, despite its exothermicity of 13.6 kcal/mol.

Experimental Section

General Methods. Melting points (uncorrected) were obtained on a Mel-Temp apparatus. Benzene, diethylhydroxylamine, styrene, thiophenol, toluene, and tetrahydrofuran were purified by distillation. The NMR solvents $CDCl_3$ and C_6D_6 from Cambridge Isotope Laboratory were used without further purification.

NMR spectra were recorded on a Bruker AC-250 with chemical shifts (δ, ppm) relative to internal TMS, hexamethyldisiloxane (^1H $\delta = 0.115$), or solvent signal ($CDCl_3$ ^1H $\delta = 7.26$, ^{13}C $\delta = 77.0$; C_6D_6 ^1H $\delta = 7.15$, ^{13}C $\delta = 128.5$). ESR spectra were run on a Varian E-12 spectrometer. Mass spectra were taken on Finnigan MAT 95 mass spectrometer. UV spectra were obtained on a Hewlett-Packard 8452A diode array spectrometer. Analytical GC was carried out on a Hewlett-Packard 5890A gas chromatograph equipped with a DB-5 capillary column (0.25 mm × 30 m) and FID. Analytical GC data were collected and manipulated on an IBM PC compatible computer. Preparative GC of **3** was attempted on an Antek 300 with a $^1/_4$ in. × 10 ft 10% FFAP on Chromosorb W column.

All samples for thermolysis were freeze−thaw degassed three times and sealed on a vacuum line. The tubes were immersed completely in a well-stirred DC-200 silicone oil bath contained in a 1.5 gallon Dewar flask. The bath temperature was regulated by a Bayley Model 123 temperature controller and was measured with a Hewlett-Packard Model 3456A digital voltmeter and a platinum thermometer. The least squares program LINFIT was used to calculate the rate constants and uncertainties for each first-order plot. The tubes were cracked open and the contents analyzed by GC with a 0.12 mm × 30 m DB-5 capillary column. The following GC conditions were used: head pressure, 16 psi; He flow at detector, 53 mL/min; injector, 210 °C; detector, 250 °C; oven initial temperature, 35 °C; initial time, 2.5 min; program rate, 10 °C/min; oven final temperature, 250 °C; final time, 10 min. All hydrocarbons were assumed to have the same weight response factor so that the GC peak areas of the products (Table 2) correspond to an approximate molar ratio of PhEt: (**10** + **11** + **13** + **14** + unknowns) of 2.25:1.00. The 23.26 min peak was assumed to be a styrene dimer.

Azo-α-phenylethane (1) was made by the method of Cohen.[8] The crude material was purified by recrystallization from ethanol at −15 °C: mp 71 °C (lit.[8] mp 72−73 °C); UV (hexane) $\lambda_{max} = 360$ nm; $\epsilon = 46$; ^1H NMR (250 MHz, $CDCl_3$) δ 1.53 (6H, d), 4.62 (2H, q), 7.38 (10H, m).

***N*-(1-phenylethoxy)diethylamine (3)**. A 250 mL three-necked flask equipped with a condenser, nitrogen inlet, and magnetic stirrer was flushed with nitrogen and charged with di-*tert*-butyl peroxide (18.75 mL, 0.1 mol) and an excess of

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(27) *Polymer Handbook*, 3rd ed., Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; p 76. Our least squares fit of $\ln(k_{prop}/T)$ versus $1/T$ gave a slope of -4357 ± 375, an intercept of 12.84 ± 1.23, and a correlation coefficient of 0.886. These values correspond to $E_a = 9.27$ kcal/mol and $\log A = 8.50$, similar to the given $E_a = 8.96$ kcal/mol, $\log A = 8.38$.

(28) The small unknown at 23.26 min was assumed to be an unsaturated styrene trimer. Of greater concern for the calculation than its actual structure is the possibility that higher styrene oligomers were not seen by GC but should be included as attack on styrene. When a solution of 0.02 M **1**, 0.02 M **2**, and 0.20 M styrene in benzene was thermolyzed at 120 °C, many GC peaks of longer retention time were observed; however, these were absent in the 0.02 M styrene experiment.

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ethylbenzene (125 mL). Diethylhydroxylamine (**2**, 10.60 mL, 0.1 mol) was added and the mixture was purged with nitrogen for 1 h before heating. The reaction mixture was brought to reflux for 7 days while the purge was continued. The excess ethylbenzene was removed by vacuum distillation. TAA **3** was obtained as a light yellow oil (500 mg, 2.6%) by flash chromatography ($R_f = 0.27$ in 5:95 ether:hexane): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.03 (6H, br t), 1.47 (3H, d), 2.70 (4H, br q), 4.71 (1H, q), 7.33 (5H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 11.9, 21.5, 52.1, 80.4, 126.9, 127.4, 128.1, 143.6; MS (70 eV) *m/e* (relative abundance) 42 (3.4), 74 (27.0), 77 (9.8), 84 (11.4), 89 (41.6), 105 (100.0), 193 (0.23); HRMS calcd for $C_{12}H_{20}NO$ (M + H) 194.1545, found 194.1543.

Diethylnitrone (12) was synthesized by the method of Murahashi.[15] To a mixture of SeO_2 (0.132 g, 0.001 mol) and diethylamine (5.28 mL, 0.05 mol) in methanol was added dropwise an aqueous 30% hydrogen peroxide solution (17.01 mL, 0.15 mol) at 0 °C under argon. After stirring at room temperature for 3 h, methanol was removed under reduced pressure. The remaining aqueous solution was extracted with dichloromethane (3 × 30 mL) and dried over with anhydrous magnesium sulfate. Flash chromatography (1:19 methanol: CH_2Cl_2) yielded light yellow liquid nitrone **12** (1.72 g, 40%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.48 (3H, t), 2.01 (3H, d), 3.83 (2H, q), 6.82 (1H, q); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 12.7, 13.2, 59.8, 134.6.

Oxazolidines 8 and 9. Nitrone **12** (0.119 g, 1.37 mmol) was heated in styrene (5 mL) under argon at 100 °C for 4 h. The solvent was evaporated and residue was subjected to flash chromatography (20:80 ether:hexane) to afford 42.3 mg of **8** ($R_f = 0.25$, 16.2%) and 62.3 mg of **9** ($R_f = 0.17$, 23.9%). **8**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.25 (6H, m), 1.94 (2H, m), 2.87 (2H, m), 3.09 (1H, br m), 5.11 (1H, t), 7.33 (5H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.2, 19.3, 46.3, 51.3, 62.5, 77.3, 126.0, 127.3, 128.3, 142.1. **9**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.25 (6H, dd), 2.32 (2H, t), 2.77 (2H, m), 2.95 (1H, br m), 5.03 (1H, t), 7.32 (5H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.3, 18.0, 45.4, 51.3, 61.7, 77.5, 126.5, 127.6, 128.4.

1,3-Diphenyl-1-butene (11) was prepared by a Wittig reaction of α-phenylpropanal with benzyltriphenylphosphorane. The latter was obtained by refluxing benzyl chloride with triphenylphosphine in toluene, followed by treatment with butyllithium. **11-E**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.41 (3H, d), 3.61 (1H, m), 6.34 (2H, d), 7.23 (10H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 21.2, 42.6, 126.1, 126.2, 127.0, 127.3, 128.5, 135.2.

1,3-Diphenylbutane (10) was synthesized by hydrogenation of the *E*,*Z* mixture of **11** over 10% Pd/C and was purified by preparative TLC: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.23 (3H, d), 1.87 (2H, m), 2.45 (2H, t), 2.65 (1H, q), 7.19 (10H, m); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 22.5, 33.9, 39.5, 40.0, 125.6, 125.9, 127.1, 128.2, 128.3, 128.4, 142.5, 147.3.

Mass Spectra of 13 and 14 (EI, 70 eV). 13: 314 (1.1), 208 (19.5), 131 (4.2), 105 (100), 91 (8.7), 79 (6.3). **14a**: 314 (16), 208(18), 196 (13), 193 (4.4), 131 (5.8), 117 (8.0), 105 (100), 91 (42), 78 (9.7). **14b**: 314 (35), 207(6.2), 196 (30), 193 (1.5), 131 (7.5), 117 (15), 105 (100), 91 (86), 78 (41).

Kinetics of Formation of Ethylbenzene and Oxazolidines from Thermolysis of 3. A 0.059 M benzene solution of **3** divided among eight sealed tubes was heated in an oil bath at 170 °C. The tubes were withdrawn periodically and analyzed by GC. Time (min), GC peak area ratio of ethylbenzene/dodecane, oxazolidines/dodecane: 15, 0.0588, 0; 20, 0.0764, 0; 30, 0.107, 0; 40, 0.155, 0.0213; 60, 0.268, 0.0581; 80, 0.311, 0.137; 110, 0.507, 0.255; 150, 0.590, 0.511.

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