Thermal Decomposition of *trans*-Dioxolane 15a and Isolation of Diperoxides 16a,b. This reaction was conducted in neat *tert*-butyl hydroperoxide with 0.82 g (2.57 mmol) of mercuric acetate. The potassium bromide step was omitted. An attempt was made to remove the *trans*-dioxolane by trap-to-trap distillation at 100 °C (0.1 mmHg). NMR analysis of the distillate showed the presence of a nearly 1:1 mixture of benzaldehyde acetophenone, but no dioxolane was found. The distillate was separated by flash chromatography on silica using CH_2Cl_2 as the eluent: benzaldehyde eluted first (R_f 0.42, CH_2Cl_2) followed by acetophenone (R_f 0.30, CH_2Cl_2). Each compound was identified by comparison of its ^1H NMR spectrum with that of an authentic sample. The residue from the distillation was column chromatographed (silica) using CH_2Cl_2 to give fractions containing varying amounts of diperoxides (**16a,b**) and *trans*-dioxolane (**15a**). The mixture was separated on an analytical HPLC unit under the conditions listed above. Fraction 1, *trans*-dioxolane (**15a**); fraction 2, meso diperoxide (**16a**); fraction 3, *d,l* diperoxide (**16b**).

meso-1,3-Bis(*tert*-butylperoxy)-1,3-diphenylpropane (**16a**): δ_H (200 MHz) 1.17 s (18 H), 2.02 dt (1 H, J = 14.1, 6.8 Hz), 2.63 dt (1 H, J = 14.1, 7.3 Hz), 4.87 t (2 H), 7.32 s (10 H); δ_C (100 MHz) 26.51, 40.02, 80.03, 82.56, 127.33, 127.79, 128.19, 140.84; MS, no molecular ion at 372, stable fragments found at m/z 226 (M^+ - *t*-BuOO - *t*-Bu) and 146 (*t*-BuOO-*t*-Bu$^+$), other fragments found at 315 (M^+ - *t*-Bu), 283 (M^+ - *t*-BuOO), 193 (PhCH=CHCHPh$^+$), 73 (*t*-BuO$^+$), and 57 (*t*-Bu$^+$).

d,l-1,3-Bis(*tert*-butylperoxy)-1,3-diphenylpropane (**16b**): δ_H (200 MHz) 1.17 s (18 H), 2.25 t (2 H, J = 6.9 Hz), 4.98 t (2 H), 7.32 s (10 H); δ_C (100 MHz) 26.51, 40.47, 80.07, 82.30, 127.12, 127.72, 128.17, 141.19; MS, no molecular ion, pattern similar to that of the meso isomer.

Inverse Addition of 0.5 equiv of Mercuric Acetate. *tert*-Butyl hydroperoxide (0.22 g, 2.45 mmol) was dissolved in dichloromethane (3 mL), and *cis*-cyclopropane **1b** (0.25 g, 1.29 mmol) and aqueous perchloric acid (3 drops) were added. Mercuric acetate (0.21 g, 0.66 mmol) was added in 13 portions to the magnetically stirred solution over a period of 4.5 h. Stirring was continued for a further 17.5 h. The reaction was worked up in the usual way. The NMR spectrum was identical with that obtained in expt 6, except for the presence of 74% unreacted cyclopropane **1b**. As a comparison, the percentage of unreacted cyclopropane was calculated by assuming that mercurials **2** and **3a,b** (C_1-C_3 scission, 19%) were derived from 1 equiv (0.070 mmol) of mercuric acetate/1 equiv (0.070 mmol) of cyclopropane, while compounds **15**, **16**, and **17** (C_1-C_2 scission, 81%) used 2 equiv (0.590 mmol) of mercuric acetate/1 equiv (0.295 mmol) of cyclopropane; calculated 0.925 mmol of unreacted cyclopropane and 0.365 mmol of products or 72% unreacted cyclopropane.

Preparation of *trans*-Dioxolane 15a. To an ice-cooled and magnetically stirred mixture of mercuric acetate (6.37 g, 20 mmol), dichloromethane (23 mL), *tert*-butyl hydroperoxide (1.71 g, 19 mmol), and aqueous perchloric acid (23 drops) was added dropwise a solution of *cis*-1,2-diphenylcyclopropane (1.94 g, 10 mmol, 90.9% pure) in dichloromethane (2 mL). The ice bath was removed, and the reaction was allowed to proceed for 22 h. Water and dichloromethane (25 mL of each) were added to the mixture. Following separation, the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The dried extracts were rotoevaporated. The mixture (3.26 g) was column chromatographed on a 45 cm × 4 cm diameter column of silica (70-230 mesh) and eluted with 1:1 petroleum ether (60-80 °C) and CH_2Cl_2. The dioxolane/diperoxide fraction began to appear after about 475 mL of eluent and was nearly all removed after another 400 mL of solvent; 0.30 g (15%) of *cis*- and *trans*-dioxolane (**15a,b**) mixed with some diperoxides (**16a,b**). Some benzaldehyde and acetophenone were observed, indicating decomposition of the dioxolanes on the column. No attempt was made to elute the organomercuric acetates. Pure *trans*-dioxolane (0.050 g) was obtained by adding petroleum ether (60-80 °C, 4 × 2 mL) to the crude dioxolane at room temperature and collecting it on a sintered funnel. The ^1H NMR spectrum was identical with that obtained on the HPLC sample (see earlier).

Kinetics of Thermal and Hydrolytic Decomposition of 1,3,4-Dioxazol-2-one Derivatives

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The synthesis of model compounds **5** and **6** for the homopolymers of vinyl- and isopropenydioxazol-2-ones is described. These compounds are hydrolyzed to hydroxamic acids which can be estimated colorimetrically by complexation with Fe^{3+}. The hydrolylitic rates have been determined and the thermolysis rates were followed by measuring undecomposed dioxazolones by the colorimetric method. The isopropyldioxazolone was 100 times faster in thermal decomposition in the bulk than the *tert*-butyl-substituted one and this difference is reduced in presence of polar solvents. The results explain the previously observed differences in the thermal stability of the two polymers.

Introduction

The synthesis of isocyanate functional polymers is of considerable interest due to the high chemical reactivity of this functional group. Poly(vinyl isocyanate) has been prepared by polymerization of vinyl isocyanate[2] and by the generation of acyl azide groups on the polymer followed by Curtius rearrangement.[3] A much more recent approach to the synthesis of isocyanates has been through the thermolytic cleavage of 1,3,4-dioxazol-2-ones.[4] Endo et al.[5] observed the generation of isocyanates on polymer backbones by the thermolysis of polymers prepared from 5-isopropenyl-1,3,4-dioxazol-2-one (**2**). The synthesis and

(1) Present address: Corporate Research Laboratories, 3M Company, St. Paul, MN 55144.

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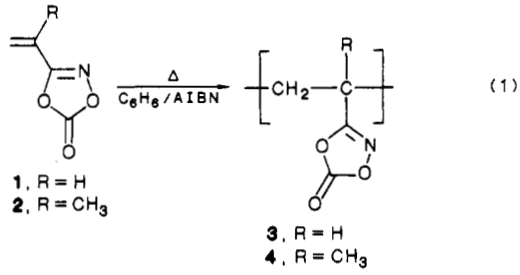
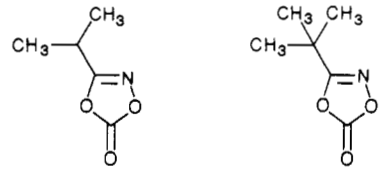
polymerization of 5-vinyl-1,3,4-dioxazol-2-one (1) has also been reported[6] and this prompted us to look in detail at the homo- and copolymerization behavior of the monomer 1.



(1)

In our studies[7] with this monomer, 1, we noted larger amounts of thermal decomposition during free radical polymerization than was observed by Endo.[5] In order to examine if polymers derived from 1 were more susceptible to thermolysis than those derived from 2, we undertook a study of the kinetics of thermal decomposition of some model dioxazolones and the results are described in this paper.

In order to compare the thermal degradation properties of the polymers 3 and 4, appropriate model systems for the two polymers had to be selected for rate studies and the derivatives 5 and 6 were chosen for this purpose.



5 6

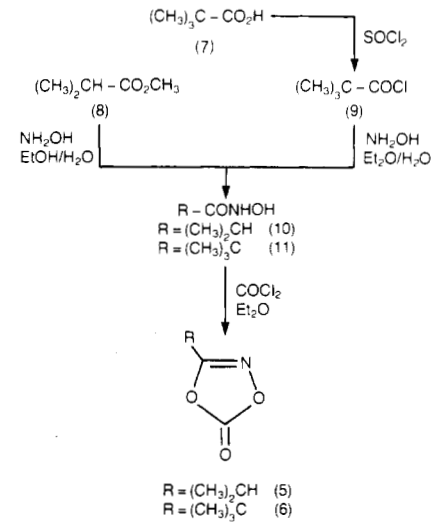
Results and Discussion

Syntheses of Models. The syntheses of model dioxazolones were accomplished by cyclization of the corresponding hydroxamic acids with phosgene (Scheme I).

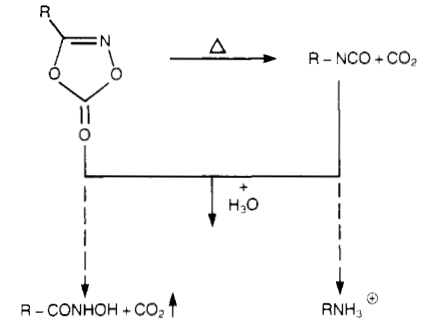
Thus, methyl isobutyrate (8) was treated with hydroxylamine in aqueous ethanol at low temperatures to convert it to isobutyrohydroxamic acid (10).[8] Pivalic acid (7) was converted to the corresponding hydroxamic acid (11) through the acid chloride (9) by the action of hydroxylamine in an aqueous ether medium. The hydroxamic acids were treated with phosgene in cold ether to give the dioxazolones 5 and 6. The formation of the dioxazolone ring in both compounds 5 and 6 was confirmed by their characteristic absorptions at 1880 and 1835 cm^{-1} in the infrared spectrum.

Kinetic Method. Manometric methods of estimating the carbon dioxide formed in the thermal decomposition of 5 and 6 were found to be difficult as the isocyanates had considerable vapor pressure in the temperature range studied. Back-titration of excess di-*ni*-butylamine that may be used to quench the isocyanate formed[10] was not possible as the 1,3,4-dioxazol-2-one ring is susceptible to nucleophilic agents like water,[11] alcohols,[12] and carboxylic

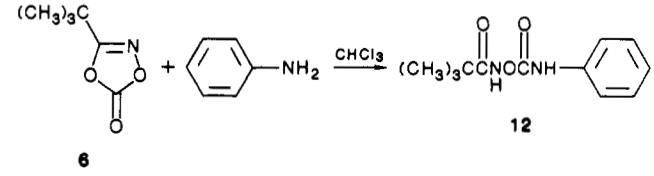
Scheme I



Scheme II



acids.[13] Nucleophilic attack by amines was established by reacting 6 with aniline, a comparatively weaker nucleophilic amine. Even at room temperature, the reaction gave about 85% of ring-opened product 12 within an hour.



6 12

The following scheme was therefore formulated to determine the reaction rates of these dioxazolones (Scheme II).

Definite weights of the starting material, with or without solvent, can be heated in sealed vials at the proper temperature for various time intervals, and the total mixture can be hydrolyzed in acidic aqueous buffers. The isocyanates formed by the reaction may be hydrolyzed under the acidic conditions to give the corresponding amine salts and the unreacted dioxazolones transformed to the corresponding hydroxamic acids. The hydroxamic acids can be converted to their colored ferric complexes which are amenable to photometric estimation.[14,15] This method can, therefore, be used to estimate the hydroxamic acid generated in our scheme if a stoichiometric relationship is established between the concentration of complex formed

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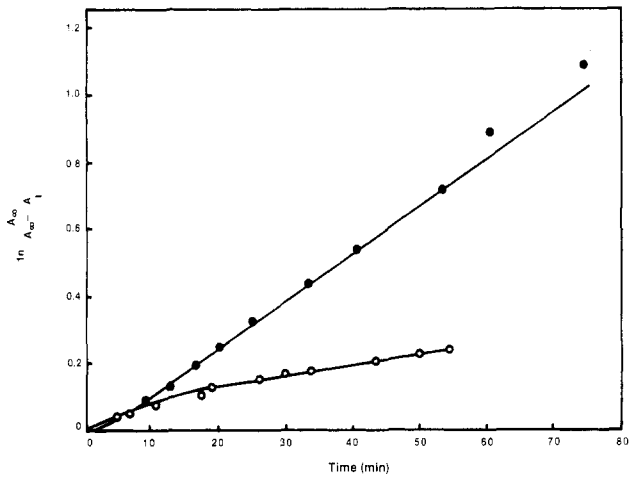

Figure 1. First-order plots of hydrolysis rates of (●) **5** and (○) methanol-treated **5** at pH 2. Concentration of Fe^{3+} = 4 × 10^{-3} M. Absorbances measured at 504 nm.

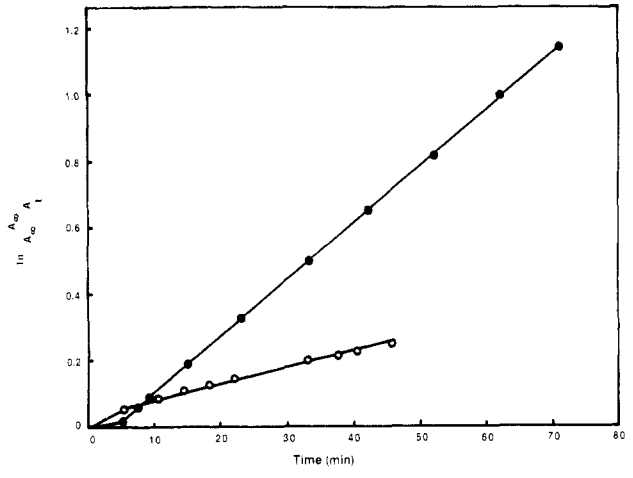

Figure 2. First-order plots of hydrolysis rates of (●) **6** and (○) methanol-treated **6** at pH 2. Concentration of Fe^{3+} = 4 × 10^{-3} M. Absorbances measured at 504 nm.

and the amount of dioxazolone from which it was generated. All complexation with Fe^{3+} was carried out at pH 2 where the 1:1 complex is favored.[16]

The hydroxamic acids **10** and **11** and the hydrolysis products of **5** and **6**, when complexed with $FeCl_3$, obey Beer's law. The hydrolyses were unaffected by the presence of isocyanates as the latter are hydrolyzed rapidly under the acidic pH conditions employed.

Hydrolytic Studies. In the hydrolyses of the dioxazolones, we allowed the reactions to proceed for 8 h before the released hydroxamic acid was complexed with Fe^{3+}. In order to ascertain that this time period was sufficient to hydrolyze all the dioxazolones used, the hydrolyses rates of **5** and **6** were studied and excellent pseudo-first-order rates were obtained (Figures 1 and 2). The rate constants were 1.45 and 1.7 × 10^{-2} min^{-1} for **5** and **6**, respectively. These values confirmed that 8 h of hydrolysis was sufficient for these materials for their estimation.

Naarman and Pohleman[17] used isopropyl alcohol as the polymerization solvent for monomers containing the dioxazolone ring. The susceptibility of this heterocycle to nucleophilic attack prompted us to examine the solvolytic

Scheme III

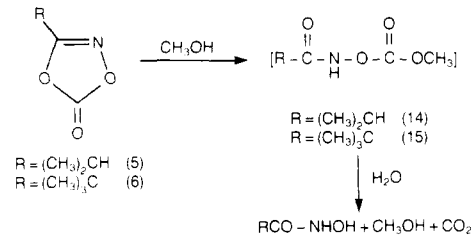

Table I. Rates and Activation Energies of Model 1,3,4-Dioxazol-2-ones

sample	solvent	temp, K	rate, h^{-1}	E_{act}, kcal/mol
5		403	1.091 × 10^{-1}	
		413	2.167 × 10^{-1}	23
		433	7.786 × 10^{-1}	
5	DMF	398	2.132 × 10^{-1}	
		410	4.435 × 10^{-1}	21.6
		420	8.637 × 10^{-1}	
5	diglyme	403	2.035 × 10^{-1}	
		413	4.130 × 10^{-1}	22.7
		423	7.910 × 10^{-1}	
6		425	5.700 × 10^{-3}	
		433	7.700 × 10^{-3}	
		443	9.800 × 10^{-3}	
6	DMF	398	9.130 × 10^{-2}	
		410	1.978 × 10^{-1}	22.0
		420	3.840 × 10^{-1}	
6	diglyme	403	4.900 × 10^{-3}	
		413	9.700 × 10^{-3}	23.5
		423	2.000 × 10^{-2}	

reaction of these dioxazolones with methanol. Known weights of the samples **5** and **6** were allowed to stir with methanol for 20 h and when aliquots of these mixtures were treated with Fe^{3+} in aqueous buffers of pH 2, no immediate coloration was observed. This ruled out the two-step solvolysis of 1,3,4-dioxazol-2-ones to hydroxamic acids by methanol. This is in contrast to the solvolysis of 1,3,2,4-dioxathiazol-2-ones which are reported[18] to be solvolyzed by alcohols to give the corresponding hydroxamic acids. However, when these aqueous buffer solutions of the mixture were allowed to stand, color slowly developed, indicating that the hydroxamic acids were being generated and the rates of the formation of hydroxamic acids were found to follow clean first-order kinetics (Figures 1 and 2). The rate constants were found to be 3.4 × 10^{-3} min^{-1} for the product derived from **5** and 4.2 × 10^{-3} min^{-1} for the product derived from **6**. Since these rates were about four times slower than the hydrolyses rates of **5** and **6**, it was therefore apparent that the treatment of **5** and **6** by methanol at room temperature had converted them, not completely to hydroxamic acids, but to "intermediates" which could later be hydrolyzed to give hydroxamic acids at a comparatively slower rate. In analogy to the case of the 1,3,2,4-dioxathiazol-2-ones,[18] we propose[19] these intermediates to be the methoxycarbonyl hydroxamates **14** and **15** (Scheme III).

Thermal Decompositions. The solvents chosen for the decomposition studies were dimethylformamide and diglyme, which are sufficiently different in polarity to allow for the observation of the effect of solvent polarity on the decomposition rates.

Weighed amounts of the samples were heated in capped vials, with or without solvent, at definite temperatures. After different time intervals, the contents of the vials were

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(19) Wolgemuth and Burk have proposed the same intermediates in the formation of isocyanates from these dioxazolones, ref 12.

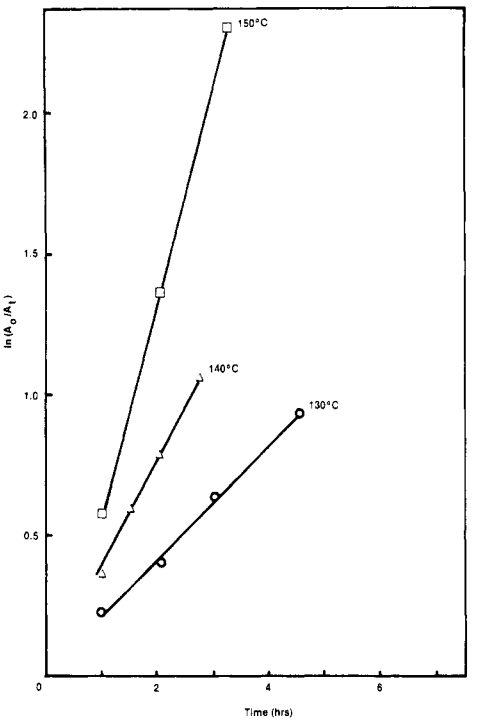

Figure 3. Arrhenius plots of thermal decomposition rates of **6** in diglyme.

thoroughly washed into aqueous KCl–HCl buffers adjusted to pH 2. After hydrolysis for 8 h, the mixtures were complexed with Fe^{3+} ions as described previously and their absorbances measured. Absorbances for zero time were calculated from the previously constructed Beer's plots and the known weights of samples. Plots of ln (A_0/A_t) against time were found to be satisfactorily linear. A typical plot is shown in Figure 3, and the first-order rate constants were determined from the slopes of these lines. The activation energies for the systems were calculated from the Arrhenius plots obtained from these rates. The rates of reactions and the activation energies are given in Table I. The Arrhenius plot of **6** in bulk was not linear and a definite activation energy could not be accurately assigned. An examination of the data reveals that **5** decomposes about 100 times faster than **6** under bulk conditions. The difference in rates is less when diglyme is used as a solvent, where **5** is about 40 times faster than **6**, and this difference is reduced further when a more polar solvent such as DMF is used. In DMF, it was found that **5** decomposes about twice as fast as **6**. In all cases, however, the *tert*-butyl derivative is found to be slower in decomposing than the isopropyl derivative. The two possible mechanisms by which this heterocycle can decompose are by either a concerted or a two-step process involving a nitrene intermediate. A more detailed study of substitution effects on reaction rates may be necessary to shed light on the relative contributions of these pathways. However, the results described in this paper explain the observation that our 5-vinyl-1,3,4-dioxazol-2-one polymers underwent faster decomposition and cross-linking than the polymers derived from 5-isopropenyl-1,3,4-dioxazol-2-one as reported by Endo.[5]

In summary, model compounds for the polymers derived from vinyl- and isopropenyldioxazolones have been prepared and their thermal decomposition rates have been studied. In the absence of polar solvents the model for the vinyl-derived polymer decomposes almost 100 times faster than that for the isopropenyl-derived polymer. Polar solvents reduce this difference.

Experimental Section

General Notes. Melting points were determined in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. Proton magnetic resonance spectra were obtained on a Varian Associates T-60 or T-60A instrument. Infrared spectra were obtained either on a Perkin-Elmer 237 or a Perkin-Elmer 437 spectrophotometer. A Beckman DU2 instrument was used for determining absorbance values for rate studies. Mass spectra were obtained on an Associated Electrical Industries MS-902 mass spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

Isobutyrohydroxamic acid (10) was prepared by the method of Fishbein et al.[8] **10**: mp 115–117 °C (lit.[8] mp 118–122 °C): ^{1}H NMR (D_2O) δ 2.4 (1 H, m), 1.2 (6 H, d); IR (KBr) cm^{-1} 3190, 1625, 1545, 1382, 1107, 1049; MS, *m/e* 103.

5-Isopropyl-1,3,4-dioxazol-2-one (5). Phosgene was passed into a well-stirred mixture of 20.6 g (0.2 mol) of isobutyrohydroxamic acid (**10**) in 400 mL of diethyl ether, maintained at a temperature between 0 °C and −10 °C. When all the suspended solid dissolved, the introduction of the phosgene was stopped and the mixture was allowed to stir at room temperature for 18 h. A small amount of precipitate appeared which was removed by filtration. The filtrate was concentrated and then distilled at 56 °C/2.25 mmHg pressure to give 23.2 g (90% yield) of 5-isopropyl-1,3,4-dioxazol-2-one (**5**): ^{1}H NMR ($CDCl_3$) δ 2.97 (1 H, m), 1.33 (6 H, d); IR (neat) cm^{-1} 2995, 1880, 1835, 1375, 1180, 1150; MS, *m/e* 129. Anal. Calcd for $C_5H_7NO_3$: C, 46.51; H, 5.43; N, 10.85. Found: C, 46.55; H, 5.43; N, 10.76.

Pivaloyl chloride (9) was prepared from the reaction between pivalic acid (**7**) and thionyl chloride by the standard procedure and was purified by being distilled three times.

Pivalohydroxamic acid (11) was prepared from pivaloyl chloride (**9**) and hydroxylamine by the method of Berndt and Schechter.[9] **11**: mp 164–165 °C (lit.[9] mp 163–164 °C); NMR (D_2O) δ 1.25 (s); IR (KBr) cm^{-1} 3270, 2982, 1618, 1525, 1407, 1380, 1240, 1070, 1030, 955; MS, *m/e* 117.

5-*tert*-Butyl-1,3,4-dioxazol-2-one (6). A suspension of 58.5 g (0.5 mol) of pivalohydroxamic acid (**11**) in 400 mL of diethyl ether was cooled to 0–10 °C and phosgene was bubbled into the mixture with stirring until all the solid dissolved. The mixture was stirred for an additional 10-h period at room temperature and filtered, and the filtrate was concentrated and distilled under vacuum; the fraction boiling at 70 °C/3.75 mmHg pressure was collected; it weighed 65.8 g (92% yield). This was characterized as 5-*tert*-butyl-1,3,4-dioxazol-2-one (**6**): NMR ($CDCl_3$) δ 1.36 (s); IR (neat) cm^{-1} 2996, 1880, 1835, 1400, 1375; MS, *m/e* 143. Anal. Calcd for $C_6H_9NO_3$: C, 50.35; H, 6.29; N, 9.79. Found: C, 50.33; H, 6.30; N, 9.77.

Reaction of 5-*tert*-Butyl-1,3,4-dioxazol-2-one (6) with Aniline. A solution of 1.43 g (10 mmol) of **6** in 10 mL of dry chloroform was stirred at room temperature with 1.12 g (12 mmol) of aniline. The mixture solidified after about 1 h; more chloroform was added to facilitate filtration and the solid residue obtained on filtration was washed successively with chloroform, petroleum ether, and water until the crystals were completely colorless; the solid was then crystallized from aqueous ethanol and dried to give 1.72 g of product. a second crop of 0.25 g of product could be isolated from the mother liquor on concentration and cooling; total yield 1.97 g (83.5%): mp, 149–150 °C with decomposition and gas evolution; NMR (DMSO-d_6) δ 7.03–7.53 (5 H, m), 1.17 (9 H, s); IR (KBr) cm^{-1} 3270, 3150, 2970, 1738, 1660, 1374, 1207. Anal. Calcd for $C_{12}H_{16}N_2O_3$: C, 61.00; H, 6.83; N, 11.86. Found: C, 61.02; H, 6.79; N, 11.87.