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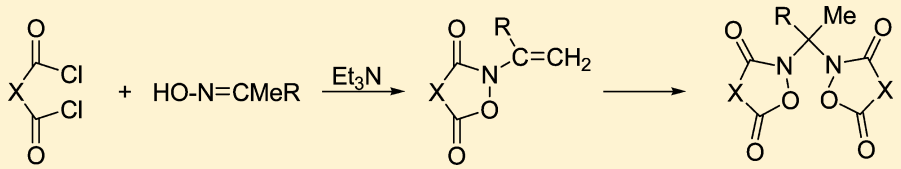
Synthesis of 3,5-Isoxazolidinediones and 1*H*-2,3-Benzoxazine-1,4(3*H*)-diones from Aliphatic Oximes and Dicarboxylic Acid Chlorides

Robert A. Izydore,*[,†] Joseph T. Jones, Benjamin Mogesa, Ira N. Swain, Ronda G. Davis-Ward, Dwayne L. Daniels, Felicia Frazier Kpakima, and Sharnelle T. Spaulding-Phifer, II

Department of Chemistry, North Carolina Central University, Durham, North Carolina 27707, United States

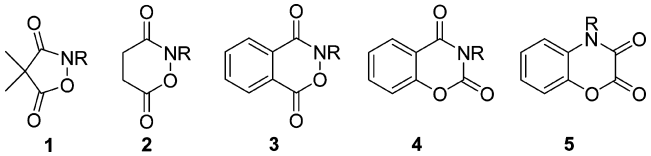
Supporting Information



ABSTRACT: The synthesis of the title compounds was carried out by reacting dicarboxylic acid chlorides with oximes in the presence of excess triethylamine. Disubstituted malonyl chlorides gave 2-alkenyl-4,4-dialkyl-3,5-isoxazolidinediones (**8a–f**) and 2,2′-ethylidene-bis[4,4-dialkyl-3,5-isoxazolidinedione]s (**9a–f**). Compounds **9** were formed from **8** and its N-unsubstituted 3,5-isoxazolidinedione decomposition product. Phthaloyl chlorides reacted with acetone oxime to yield 3-(1-methylethenyl)-1*H*-2,3-benzoxazine-1,4(3*H*)-diones (**16a–e**). Products **16** spontaneously decomposed to give N-unsubstituted 1*H*-2,3-benzoxazine-1,4(3*H*)-diones (**17a–e**) at rates that were dependent on temperature and solvent. Kinetic studies showed that two of the compounds decomposed by zero-order kinetics under neutral conditions. Butanedioyl chloride did not produce a cyclic product.

INTRODUCTION

The 3,5-isoxazolidinediones (**1**) are an important pharmacologically active class of compounds. We have shown that they are potent hypolipidemic[1−5] and cytotoxic[6] agents, specific inhibitors of the type-2 isoform of IMPDH,[7] and inhibitors of aldose reductase.[8,9] They also act as antidiabetic agents.[10−15] Six-membered ring analogues of **1** include the 2*H*-1,2-oxazine-3,6-diones (**2**) and the 1*H*-2,3-benzoxazine-1,4(3*H*)-diones (**3**).[16−25] While there has been one report each on the fungicidal properties[23] and the *β*-Lactamase pro-inhibitory activity[26] of **3**, the pharmacological properties of **2** and **3** have been largely unexplored. In contrast, the corresponding 2*H*-1,3-benzoxazine-2,4(3*H*)-diones (**4**) have a wide range of pharmacologic activities including antimycobacterial,[27−31] antituberculotic,[32−36] analgesic,[37,38] cardiovascular,[39] antimitotic,[40] antifungal,[41,42] cytotoxic,[43] and antifungal,[44] and the 2*H*-1,4-benzoxazine-2,3(4*H*)diones (**5**) are active as antimitotic,[40] antimicrobial,[45] antiallergic,[46,47] and renin inhibitory[48] agents. It appears likely then that **2** and **3** would also have useful pharmacological activities.



As part of our ongoing investigation into the pharmacological activities of 3,5-isoxazolidinediones and related ring systems, it was of interest to investigate the synthesis of *N*-alkenyl derivatives of **1**, **2**, and **3**. We reported previously that addition of dimethyl (**6a**) and diethylmalonyl chloride (**6b**) to ether solutions of acetone oxime (**7a**) and triethylamine gave 2-(1-methylethenyl)-3,5-isoxazolidinediones (**8a** and **8b**) and 2,2′-(1-methylethylidene)bis[4,4-dialkyl-3,5-isoxazolidinedione]s (**9a** and **9b**). Also formed were small amounts of N-unsubstituted 3,5-isoxazolidinediones (**10a** and **10b**) and *O*,*O*′-(2,2-dialkyl-1,3-dioxo-1,3-propanediyl)dioxime 2-propanones (**11a** and **11b**) (Scheme 1).[49] Products **8a** and **8b** represent the only examples of 2-alkenyl-3,5-isoxazolidinediones reported to date. Mechanisms for the formation of products **8** and **9** were proposed. In simple terms products **8** can be considered to arise by the condensation of the oxime with **6** followed by base-promoted ring closure of the monooxime ester. Compounds **8b** and **9b** were subsequently shown to give moderate lowering of blood serum cholesterol and serum triglyceride levels in CF_1 mice when administered for 16 days at a dosage of 20 mg/kg/day ip.[1,2]

Because only a limited number of derivatives of **8** and **9** were obtained, we explored in this study additional reactions between **6** and **7** in order to gain insight into the scope of the reaction. We also investigated the unreported reactions of phthaloyl and butanedioyl chlorides, respectively, with oximes to determine if they would react similarly to **6**. Reported herein are the results of these investigations.

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Scheme 1. Reactions of Substituted Malonyl Chlorides with Oximes

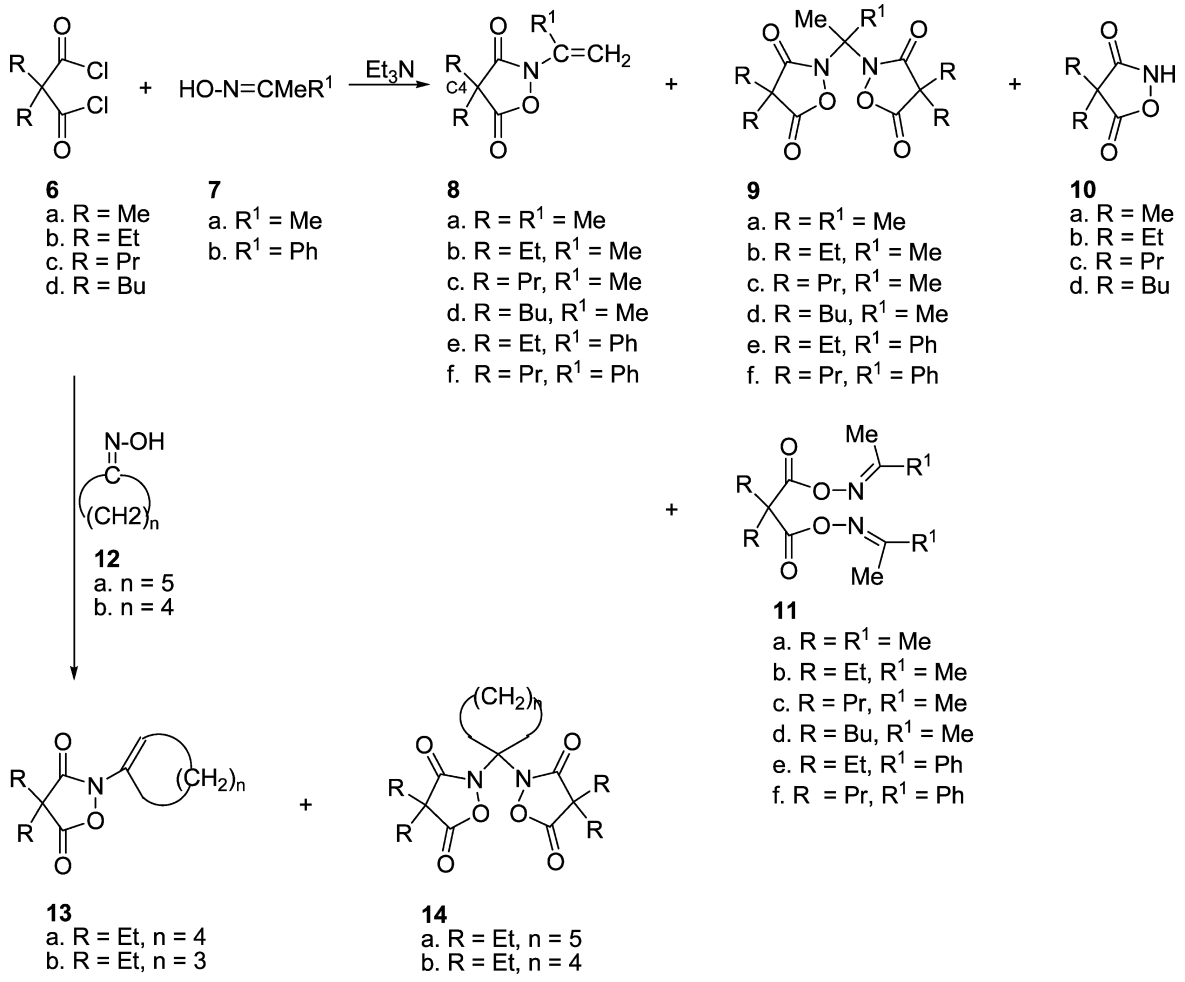

Table 1. Reactions of Dialkylmalonyl Chlorides (6) with Oximes (7)

		percent yield[a]					
acid chloride	oxime	8	9	10	11	13	14
6a	**7a**	**8a** (29[b,c,d])	**9a** (25[b,c,d])	**10a** (2[b,c])	**11a** (tr[b,c])		
6b	**7a**	**8b** (23[b])	**9b** (51[b])	**10b** (tr[b])	**11b** (tr[b])		
6c	**7a**	**8c** (22)	**9c** (28)	**10c** (5)	**11c** –		
		8c (28[e])	**9c** (18[e])	**10c** (11[e])			
6d	**7a**	**8d** (tr)	**9d** (40)	**10d** (12)	**11d** –		
		8d (22[e])	**9d** (30[e])	**10d** (17[e])			
6b	*E*-**7b**	**8e** (45)	**9e** (16)	**10b** –	**11e** –		
6c	*E*-**7b**	**8f** (18)	**9f** –	**10c** –	*E*,*E*′-**11f** (40)		
6b	**12a**					**13a** (62[f])	**14a** –[f]
						13a (2[g])	**14a** (35[g])
6b	**12b**					**13b** –	**14b** (16)

[a]Except where noted, the reactions were carried out by adding **6** to an ether solution of **7** and a 50% excess of Et_3N at 0 °C and then stirring at rt for 20 h. [b]Reference 42. [c]A stoichiometric quantity of Et_3N was used. [d]Yield revised from reference 42. [e]**7a** was added to an ether solution of **6** and Et_3N. [f]Initial yield by HPLC. [g]Yield by HPLC after 72 h.

RESULTS AND DISCUSSION

Reactions of malonyl chlorides with a variety of oximes were investigated. In our previous study we observed that the stability of compounds **8** was related to the steric size of the substituents at position-4 of the ring and followed the order Et > Me > H. Both **8a** and **8b** were stable to distillation under reduced pressure, but when stored at room temperature, **8b** was indefinitely stable, whereas **8a** slowly decomposed over several months. Compound **8** (R = H) was too unstable to be isolated. Higher yields of **8b** and **9b** were obtained when the reactions were carried out in the presence of a 50% excess of Et_3N.[49] Accordingly, the reactions in the current study were generally carried out using this excess.

Dipropylmalonyl chloride (**6c**) was added to an ether solution of acetone oxime (**7a**) in the presence of excess Et_3N at 0 °C, and the mixture was stirred for 20 h at room

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temperature to give **8c**, **9c**, and **10c**, respectively (Table 1). When the reaction was carried out with inverse addition under the same conditions, i.e., by adding **7a** to an ether solution of **6c** and Et_3N, the yields of **8c** and **10c** increased slightly, whereas that of **9c** decreased. In a similar manner dibutylmalonyl chloride (**6d**) reacted with **7a** to yield **8d**, **9d**, and **10d**. The yield of **8d** was negligible in the standard addition but increased substantially, along with a decreased yield of **9d** and an increased yield of **10d**, in the inverse addition. There was no evidence of bis-oxime ester formation (**11c** or **11d**) in either of the two reactions. Compound **8c** was stable to heating at 56 °C for 3.5 h. Both **8c** and **8d** were indefinitely stable at room temperature.

The reaction of **6b** with (*E*)-acetophenone oxime (**7b**) produced both **8e** and **9e** but no **10b** or **11e**. Compound **8e** was stable at room temperature but thermally unstable to vacuum distillation, giving a complex mixture that showed no vinyl hydrogen signals in its ^{1}H NMR spectrum. The yields of **8e** and **9e** varied with the amount of base used. When the reaction was carried out with a stoichiometric quantity of Et_3N, the yields of **8e** and **9e** were 36% and <1%, respectively. However, using a 50% excess of Et_3N caused the yield of **8e** to increase slightly (39%) and the yield of **9e** to increase to 10%, similar to that observed for **8b** and **9b**. Compound **9e** showed separate ^{1}H NMR signals for the isoxazolidinyl ethyl groups due to its asymmetry. Its mass spectrum was typical of compounds **9** in general in that it did not show a molecular ion peak but gave instead a peak corresponding to cleavage of one of the isoxazolidine rings.[50] The corresponding reaction of **6c** with *E*-**7b** produced a little **8f** but no **9f** or **10c**. Instead *E*,*E*′-**11f** was obtained as the major product. Apparently the presence of the larger propyl groups retards ring closure of the initially formed monooxime ester to **8f** and promotes diesterification of **6c**. The stereochemistry of **11f** has been assigned as *E*,*E*′ because it was formed from *E*-**7b** and its ^{13}C NMR spectrum shows the oximyl methyl groups at δ 14.4. The corresponding methyl groups of the *Z*,*Z*′-isomer or one of the methyl groups of the *E*,*Z*-isomer are expected to appear near δ 26.[51]

The reaction of **6b** with cyclic oximes was studied. Cyclohexanone oxime (**12a**) reacted with **6b** to yield initially **13a** (62%) and no **14a** as shown by ^{1}H NMR and HPLC analysis of the isolated product mixture. Compound **13a** was thermally unstable at room temperature and gradually decomposed over 72 h to give partial conversion to **14a** (35%) and several unidentified decomposition products. Only 2% of **13a** remained. It is probable that **10b** was an intermediate in the conversion.[49] Intermediate **10b** was likely formed in the same manner as compounds **17** (see discussion below). The overall process would involve partial decomposition of **13a** to **10b** followed by addition of the NH bond of **10b** across the alkenyl double bond of **13a**. The exact mechanism for the addition step is not known.

In a similar manner cyclopentanone oxime (**12b**) reacted with **6b** to produce **14b**, but **13b** was not obtained. Based on the behavior observed in the corresponding reaction of **12a**, it is likely that **13b** was formed but was not stable enough for isolation or detection.

Phthaloyl chloride (**15a**) reacted with **7a** in the presence of triethylamine to yield 3-(1-methylethenyl)-1*H*-2,3-benzoxazine-1,4(3*H*)-dione (**16a**) and the N-unsubstituted 1*H*-2,3-benzoxazine-1,4(3*H*)-dione (**17a**)[52,53] (Scheme 2). There was no evidence for the presence of the 2,2-bis(2,3-benzoxazine-1,4-dione)propane **18** or bis-acetoneoxime phthalate **19** (Table 2).

Scheme 2. Reaction of Phthaloyl Chlorides with 7a

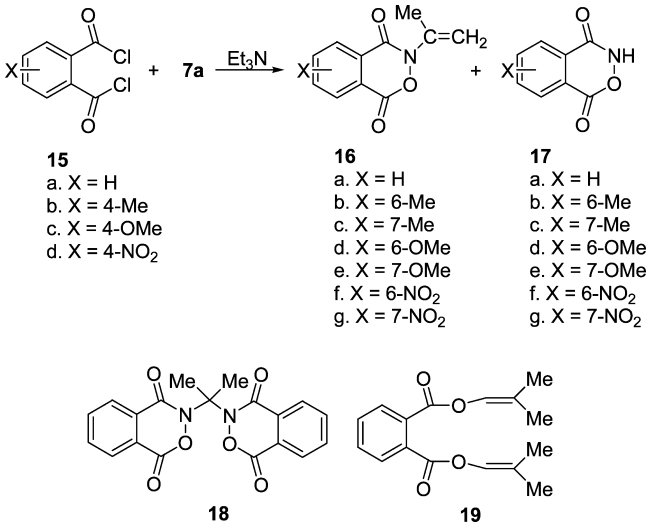

Table 2. Reaction of Phthaloyl Chlorides (15) with 7a

		percent yield[a]	
acid chloride	oxime	16	17
15a	**7a**	**16a** (74)	**17a** (11)
15b	**7a**	**16b**, **16c** (76)	**17b**, **17c** (0)
15c	**7a**	**16d**, **16e** (30)	**17d**, **17e** (<1)
15d	**7a**	**16f**, **16g** –	**17f**, **17g** –

[a]The reactions were carried out by adding **15** to an ether solution of **7a** and a 50% excess of Et_3N at 0 °C and then stirring at rt for 24 h.

An attempt to prepare **16a** by reacting phthalic anhydride with **7a** gave only unreacted starting materials. The reaction between 4-methylphthaloyl chloride (**15b**) and **7a** gave a mixture containing the 6-methyl- and 7-methyl-3-alkenyl-1*H*-2,3-benzoxazine-1,4-diones (**16b** and **16c**). No **17b** or **17c** was isolated. The presence of the two isomers was demonstrated in the ^{1}H NMR spectrum, which showed four vinyl hydrogen signals and two methyl singlets (58:42) at δ 2.58 and δ 2.56, respectively. Attempts to separate the two isomers by column chromatography or analytical HPLC were unsuccessful. In a similar manner 4-methoxyphthaloyl chloride (**15c**) reacted with **7a** to produce a nearly equimolar mixture containing the 6-methoxy- and 7-methoxy-3-alkenyl-1*H*-2,3-benzoxazine-1.4-diones (**16d** and **16e**). Two methoxy singlets (52:48) appeared in the ^{1}H NMR spectrum at δ 3.89 and 3.87, respectively. 3-Nitrophthaloyl chloride (**15d**) reacted with **7a** to give a complex product mixture. The presence of **16f** and **16g** was not detected in the ^{1}H NMR spectrum of the mixture, which showed no vinyl hydrogens, and there was no evidence for the formation of **17f** and **17g**. It is possible that the presence of the strong electron-withdrawing nitro group caused the initially formed *N*-alkenyl products **16f** and **16g** to be too unstable for isolation.

Compound **16a** was found to be thermally unstable. A sample of pure **16a** gradually and completely decomposed in a sealed glass vial at room temperature over 3 months to yield **17a**. Therefore, the decomposition was spontaneous at room temperature. Similarly, a mixture of 6-methyl- and 7-methyl-1*H*-2,3-benzoxazine-1,4-dione **17b** and **17c** was obtained by allowing the mixture of **16b** and **16c** to partially decompose at room temperature over 2 weeks (33% conversion by HPLC).

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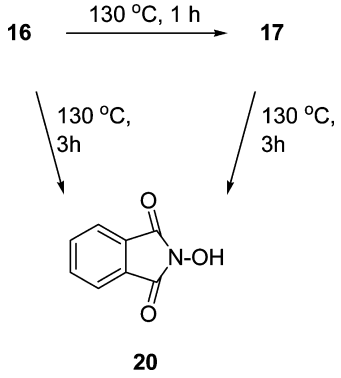
Two methyl singlets (52:48) appeared in the ^{1}H NMR spectrum at δ 2.60 and 2.58, respectively. Compound **16a** decomposed to give **17a** (98%) and *N*-hydroxyphthalimide (**20**) (2%) when it was heated under nitrogen at 130 °C for 1 h. Continued heating for an additional 2 h at 130 °C yielded **20** (99%) and **17a** (1%) (Scheme 3). Attempts to purify **16a** by

Scheme 3. Thermal Decomposition of 16



recrystallization from hot cyclohexane led to partial conversion to **17a**, and this continued each time the recrystallization was repeated. The formation of **17** by the thermal decomposition of **16** represents an improved and efficient method for its formation compared to the previously reported synthetic route.[52,53] It has an advantage in that the loss of the *N*-alkenyl substituent of **16** occurs under neutral and relatively mild thermolytic conditions, so the use of acid, base, or high temperature is avoided. Thus acetone oxime appears to be a good reagent for converting phthaloyl chlorides to **17**. It should be noted that compounds **17** cannot be prepared directly from **15** and hydroxylamine; *N*-hydroxyphthalimide is formed instead.[52−54]

Compound **16a** was found to be stable in absolute EtOH/CH_2Cl_2 (80:20) at room temperature for 30 h. A solution (4.9×10^{-2} M) of **16a** in MeCN/water (75:25) at room temperature showed virtually no decomposition after 1 h and slight decomposition to **17a** (8%) after 10 h as shown by HPLC analysis. The decompositions were much more rapid when the solution was heated at reflux, giving **17a** (93%) and **20** (7%) after 1 h and **17a** (7%) and **20** (89%) after 10 h. The decomposition behavior observed in the refluxing solvent system was very similar to that observed from heating **16a** at 130 °C under N_2. This suggests that the decompositions occurred by the same mechanism under the two different conditions.

The relative stabilities of **16a**, **16b,c**, and **16d,e** were compared in refluxing MeCN/water solutions under neutral conditions [MeCN/water (70:30)], acidic conditions [MeCN/water/chloroacetic acid (68:29:3)], and basic conditions [MeCN/water/pyridine (67:29:4)]. The reactions were monitored by HPLC, and data were taken at 15 min intervals. Kinetic plots of concn vs time, ln concn vs time, and 1/concn vs time were made to determine the reaction orders. The kinetic plots showed that under the neutral conditions **16a** and **16b,c** decomposed by zero-order kinetics, whereas **16d,e** decomposed by first-order kinetics. All of the compounds decomposed by first-order kinetics under the acidic and basic conditions.[55] Table 3 shows the decomposition half-lives and the square of the linear correlation coefficients (r^2) for the three

Table 3. Thermal Decomposition of 3-(1-Methylethenyl)-1*H*-2,3-benzoxazine-1,4(3*H*)-diones (16) in Refluxing MeCN/Water Solutions[a]

		$t_{1/2}$ (min) (r^2)		
compound	concn ($M \times 10^3$)[a]	neutral conditions[b]	acidic conditions[c]	basic conditions[d]
16a	4.9	135[e] (0.993)	38[f] (0.978)	9[f] (0.999)
16b,c	4.6	480[e] (0.984)	50[f] (0.982)	10[f] (0.996)
16d,e	4.3	57[f] (0.998)	40[f] (0.998)	35[f] (0.991)

[a]The solutions were prepared by dissolving 0.020 g of each compound in 20 mL of the appropriate solvent system. [b]MeCN/water (70:30). [c]MeCN/water/chloroacetic acid (68:29:3). [d]MeCN/water/pyridine (67:29:4). [e]Zero-order reaction. [f]First-order reaction.

sets of compounds under the different decomposition conditions. All of the r^2 values are high, indicating a high probability for a linear correlation. Alkaline and acidic conditions enhanced the rate of decomposition, with basic conditions having a more pronounced effect. Overall the three compounds were most stable under neutral conditions and least stable under alkaline conditions. Under neutral conditions the order of stability of the three compounds appears to parallel their expected hydrophilicities. Factors such as polarity, hydrogen bonding, hydrophilicity, acid−base interactions, and other factors might make contributions to the observed relative rates. We will not speculate on the relative importance of these factors among the three compounds. However, it is important to emphasize that compounds **16** have *N*-alkenyl substituents on a resonance-stabilized amide type of nitrogen, so it is not surprising that these compounds did not show behavior consistent with those of enamines. Enamines would be expected to be more stable under alkaline and neutral conditions and less stable under acidic conditions.

Reactions exhibiting zero-order kinetics are relatively uncommon. This order is most often observed in photochemical reactions, heterogeneous reactions, and enzyme-catalyzed reactions.[56] Heterogeneous reactions involving a solid catalyst and enzyme-catalyzed reactions are found to be first order with respect to the catalyst or enzyme and zero order with respect to the substrate. This is because the rate of these reactions is determined by the concentration of the catalyst or enzyme, provided that the substrate is in sufficient excess. The zero-order rates exhibited by **16a** and **16b,c** are significantly slower than those of the first-order reactions. These compounds are less reactive than **16d,e** under neutral conditions, implying different mechanisms. A plausible explanation for the zero-order reactions is that they occurred by catalysis on active sites on the surface of their glass reaction containers, and the number of these active sites was relatively small compared to the concentration of the compounds. In contrast, the first-order reactions are spontaneous thermally induced reactions. They are enhanced under acid or base catalysis or in the case of **16d,e** by the electron-releasing methoxy group.

It is likely that either propyne or allene was evolved during the decompositions. Attempts to form a mercuric derivative of the evolved gas by the procedure of Johnson and McEwen gave a solid whose melting point indicated that dipropynyl mercury might be present.[57] When 0.3 mmol of **16b,c** was allowed to stand at 70 °C for 1 h in a sealed IR gas cell, no IR discernible absorptions were observed. However, when the gas cell was kept at 70 °C for 24 h, 13% decomposition occurred, and a

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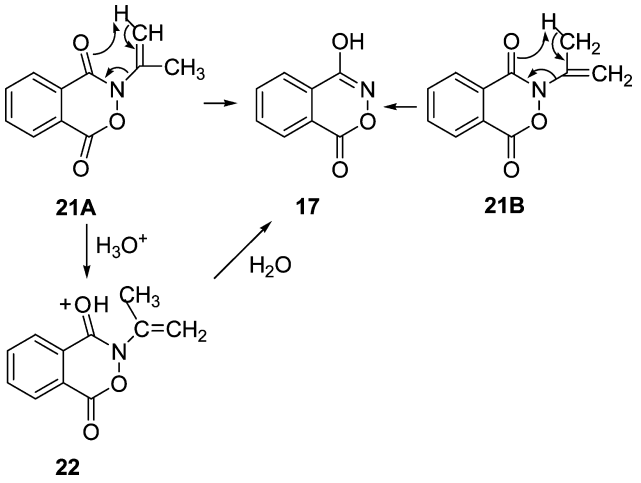
FTIR spectrum identical to that of pure acetone vapor was obtained. There was no evidence for the presence of either propyne or allene. In a separate experiment **16a** was allowed to decompose in a sealed flask that was first purged with nitrogen at room temperature for 1 h and then evacuated to 55 Torr. The flask was submerged in an oil bath maintained at 125 °C while **16a** partially decomposed over 30 min. After cooling, a volume of the headspace gas was removed and analyzed by GC−MS. In addition to atmospheric gases only acetone was observed to be present.

The decomposition of **16a** can be depicted as an intramolecular β-elimination of either propyne from **21A** or allene from **21B** (Scheme 4). In terms of thermodynamic stability

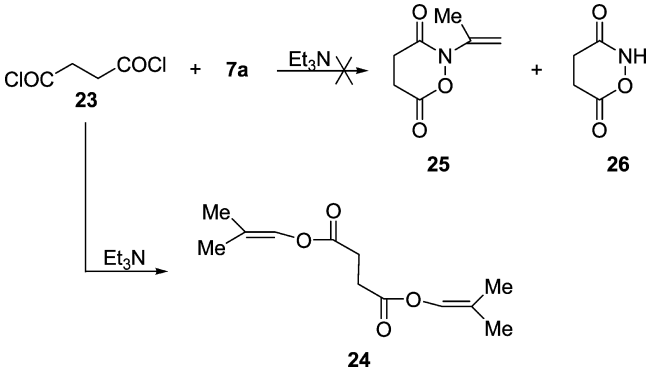
Scheme 4. Decomposition Modes of 3-(1-Methylethenyl)-1*H*-2,3-benzoxazine- 1,4(3*H*)-diones



propyne is expected to preferentially form because its experimental heat of formation is more favorable by 5.5−5.6 kJ/mol than that of allene.[58,59] Although difficulties have been experienced in obtaining accurate C−H bond dissociation energies of simple alkanes and alkenes, the C−H bond dissociation energy of ethylene is reported to be 91−116 kJ/mol greater than that of the allylic C−H bond of propene at 298 K.[60,61] No experimental values for bond dissociation energies for the vinyl C−H bonds of propene have been published, but ab initio STO-3G calculations have suggested that the bond dissociation energies of the vinylic CH_2 bonds of propene are within a few percent of the ethylene value.[62−64] These bond dissociation energy values argue for the preferred formation of allene via **21B** provided that the decomposition is governed by kinetic control. It is well established that propyne and allene exist as an equilibrium mixture. At 298 K the equilibrium constant (K_{eq}) for the isomerization of allene to propyne is 24.74.[63] This corresponds to a gas phase mixture containing 96.1% propyne and 3.9% allene. In the decompositions carried out in the refluxing solvent systems and at 130 °C equilibrium was probably established fairly rapidly, and if allene was initially or partially formed, it likely isomerized quickly to propyne. It is possible that the acetone was formed by hydration of propyne (or allene) with water that was adsorbed on the surface of the glass. Glasses are known to contain dissolved hydroxyl species and water.[65−68] Propyne and other alkynes are known to react with hydroxyl radical at 253−343 K by an addition mechanism.[69,70] Alkenes can also be hydrated in the gas phase.[71−73] Although it is not known with certainty how the acetone was formed, its presence is consistent with the loss of a three-carbon atom fragment from **16a**. In the catalyzed decomposition reactions carried out in MeCN/water, the presence of pyridine would serve to enhance the rate of β-elimination from **21A** or **21B** by offering a competing pathway for its occurrence. The presence of chloroacetic acid would allow for the formation of **16A** by β-elimination via **22**.

The reaction between **7a** and butanedioyl chloride (**23**) in the presence of triethylamine was investigated to determine if the 3-alkenyl-2,3-oxazine-1,4-dione (**25**) would be produced. Neither the 3-alkenyl-2,3-oxazine-1,4-dione (**25**) nor the N-unsubstituted bis-2,3-2*H*-1,2-oxazine-3,6-dione (**26**) was formed (Scheme 5). The bis-dimethylketoximyl butanedioate

Scheme 5. Reaction of Butanedioyl Chloride and 7a



(**24**) was formed instead. Compound **23** apparently reacted in its preferred *anti* conformation. The initially formed monoester did not undergo cyclization but underwent diesterification to yield **24**. Diacid chlorides having carbon chains longer than four carbons would also be expected to give diesterified products.

Scheme 6 suggests the reaction pathways that are followed in the reactions that we have investigated involving acetone oxime with diacid chlorides. Initial reaction between **27** and **7a** gives the monoxime ester **28**, which can either lose methyl hydrogen to triethylamine and undergo ring closure to **30** or react with a second molecule of **7a** to form **29**. When X corresponds to one disubstituted sp^3 hybridized carbon atom or *ortho*-disubstituted aromatic carbons, **30** is produced. In the former instance the reactions are sensitive to the size of the substituents both at position-2 of the malonyl chlorides and on the oxime. When X corresponds to two (and presumably more than two) sp^3 hybridized carbons, dioxime esters **29** are formed. Compounds **30** are thermally unstable and spontaneously decompose at varying rates with loss of propyne and possibly allene to yield **31**. Once formed compounds **31** can add to **30** to produce **32**. This can occur under the reaction conditions or after **30** has been isolated as shown by the conversion of **13a** to **14a**. Compounds **32** are stable. The production of **32** does not occur in the reactions involving phthaloyl chlorides.

EXPERIMENTAL SECTION

General Procedure for the Reaction of Dialkylmalonyl Chlorides (6) with Oximes (7). To a solution of 25 mmol of oxime (**7** or **12**) and 75 mmol of Et_3N in 70 mL of anhydrous Et_2O at 0 °C was added dropwise over 15 min 25 mmol of dialkylmalonyl chloride (**6**). The reaction mixture was allowed to warm to rt and then stirred under N_2 for 20 h. The white precipitate was filtered, and the filtrate was washed with HCl (10%, 3 × 25 mL) and then dried ($MgSO_4$). The Et_2O solution was dried ($MgSO_4$) and evaporated

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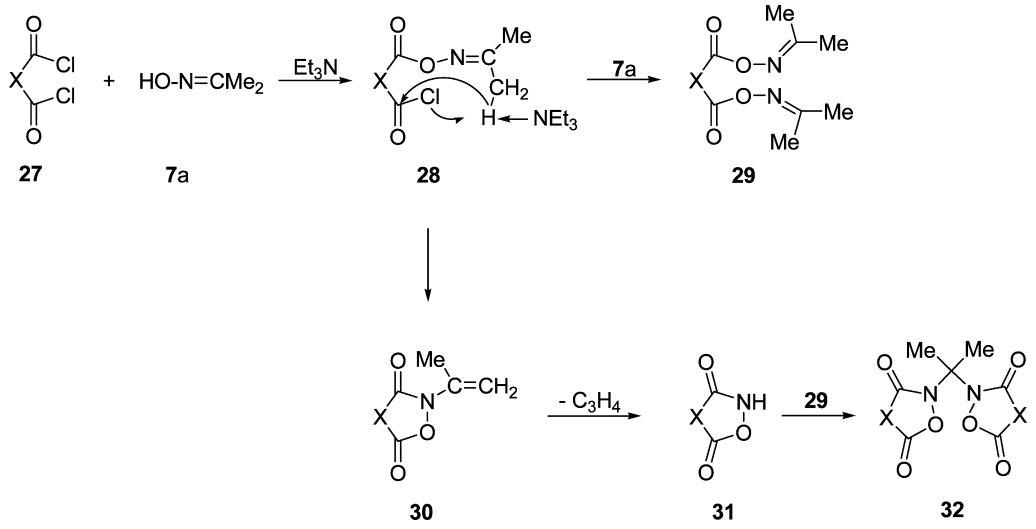
Scheme 6. Reaction Pathways Followed in the Reaction of Diacid Chlorides with Oximes



under reduced pressure. The residue was purified by column chromatography over silica gel (230−400 mesh) using hexane/EtOAc (97:3).

4,4-Dipropyl-2-(1-methylethenyl)-3,5-isoxazolidinedione (8c). Reaction of 27 mmol of diacid chloride gave a colorless oil: yield 1.35 g, 22%, IR (neat) 1821, 1726, 1641 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 5.02 (s, 1H), 4.60 (s, 1H), 2.21 (s, 3H), 1.82 (m, 4H), 1.31 (m, 4H) and 0.92 (t, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 13.8, 18.0, 19.6, 37.9, 53.1, 100.3, 136.4, 167.7, 172.2; HRMS m/z $[M + H]^+$ calcd for $C_{12}H_{20}NO_3$ 226.1444, found 226.1446; HRMS m/z $[M + Na]^+$ calcd for $C_{12}H_{19}NO_3Na$ 248.126, found 248.126. Reaction of 25 mmol of diacid chloride using inverse addition gave 1.56 g, 28% of **8c**.

2,2′-(1-Methylethylidene)bis[4,4-dipropyl-3,5-isoxazolidinedione] (9c). Reaction of 27 mmol of diacid chloride using inverse addition gave a colorless viscous liquid which solidified on standing: yield 1.54 g, 28%; mp 74−76 °C (LB pet ether); IR (neat) 1817 (s), 1738 cm^{-1} (s); ^1H NMR (300 MHz; $CDCl_3$) δ 2.09 (s, 6H), 1.74 (m, 8H), 1.31 (m, 8H), and 0.92 (t, 12H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 13.9, 17.9, 25.7, 37.7, 53.2, 78.8, 170.5, 171.9; HRMS m/z $[M + K]^+$ calcd for $C_{21}H_{34}N_2O_6K$ 449.2055, found 449.2037. Anal. Calcd for $C_{21}H_{34}N_2O_6$: C, 61.44; H, 8.35; N, 6.82. Found: C, 61.37; H, 8.24; N, 6.71. Reaction of 25 mmol of diacid chloride using inverse addition gave 0.90 g, 18% of **9c**.

4,4-Dipropyl-3,5-isoxazolidinedione (10c). Reaction of 27 mmol of diacid chloride gave a colorless viscous liquid: yield 0.25 g, 5%; IR (neat) 1817, 1738 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 8.54 (br s, 1H), 1.80 (m, 4H), 1.31 (m, 4H), and 0.92 (t, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 13.8, 17.9, 37.4, 51.6, 174.6, 175.7; HRMS m/z $[M + Na]^+$ calcd for $C_9H_{15}NO_3Na$ 208.0950, found 208.0948. Reaction of 25 mmol of diacid chloride using inverse addition gave 0.50 g, 11% of **10c**.

4,4-Dibutyl-2-(1-methylethenyl)-3,5-isoxazolidinedione (8d). Reaction of 20 mmol of diacid chloride using inverse addition gave a colorless viscous liquid: yield 1.12 g, 22%; IR (neat) 1820, 1728, 1642 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 5.04 (s, 1H), 4.60 (s, 1H), 2.22 (s, 3H), 1.83 (m, 4H), 1.28 (m, 8H) and 0.90 (t, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 13.7, 19.6, 22.5, 26.6, 35.7, 53.0, 100.3, 136.5, 167.8, 172.2; HRMS m/z $[M + H]^+$ calcd for $C_{14}H_{24}NO_3$ 254.1751, found 254.1755; HRMS m/z $[M + Na]^+$ calcd for $C_{14}H_{23}NO_3Na$ 276.156, found 276.158.

2,2′-(1-Methylethylidene)bis[4,4-dibutyl-3,5-isoxazolidinedione] (9d). Reaction of 18 mmol of diacid chloride gave a colorless viscous liquid that solidified on standing: yield 1.70 g, 40%; mp 67−68 °C (LB pet ether); IR (neat) 1822, 1735 cm^{-1} (s); ^1H NMR (300 MHz; $CDCl_3$) δ 2.10 (s, 6H), 1.79 m, 8H), 1.30 (m, 16H), and 0.89 (t, 12H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 13.6, 22.6, 25.7, 26.5, 35.4, 53.0, 78.8, 170.5, 171.8; HRMS m/z $[M + H]^+$ calcd for $C_{25}H_{43}N_2O_6$ 467.3116, found 467.3105; HRMS m/z $[M - C_{11}H_{18}NO_3]^+$ calcd for $C_{14}H_{24}NO_3$ 254.1757, found 254.1766; HRMS m/z $[M + K]^+$ calcd for $C_{25}H_{42}N_2O_6K$ 505.2674, found 505.2676. Reaction of **20** mmol of diacid chloride using inverse addition gave 1.39 g, 30% of **9d**.

4,4-Dibutyl-3,5-isoxazolidinedione (10d). Reaction of 18 mmol of diacid chloride gave a colorless viscous liquid: yield 0.46 g, 12%; 230−400 mesh silica gel (hexane/EtOAc (80:20)); IR (neat) 1817, 1737 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 10.25 (br s, 1H), 1.84 m, 4H), 1.30 (m, 8H), and 0.89 (t, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 13.6, 22.5, 26.6, 35.1, 51.5, 174.3, 176.0; HRMS m/z $[M + Na]^+$ calcd for $C_{11}H_{19}NO_3Na$ 236.1263, found 236.1248; HRMS m/z $[M + K]^+$ calcd for $C_{11}H_{19}NO_3K$ 252.1003, found 252.0985. Reaction of **20** mmol of diacid chloride using inverse addition gave 0.73 g, 17% of **10d**.

4,4-Diethyl-2-(1-phenylethenyl)-3,5-isoxazolidinedione (8e). Reaction of 20 mmol of diacid chloride gave a colorless viscous liquid: yield 2.32 g, 45%; 60−200 mesh silica gel ($CHCl_3$/hexane (98:2)) or 50 cm ODS-2 HPLC column (MeCN/water (60:40)); IR(neat) 1816(s), and 1721(s) cm^{-1} (s); ^1H NMR (60 MHz; $CDCl_3$) δ 7.30 (s overlapping a small m, 5H), 5.47 (s, 1H), 5.34 (s, 1H), 1.83 (q, 4H), and 0.91 (t, 6H); MS m/z (rel intensity) 259 (44), 215 (48), 199 (85), 108 (89) and 106 (100); HRMS m/z $[M]^+$ calcd for $C_{15}H_{17}NO_3$ 259.1208, found 259.1209. Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.64; H, 6.91; N, 5.04.

2,2′-(1-Phenylethylidene)bis[4,4-diethyl-3,5-Isoxazolidinedione] (9e). Reaction of 20 mmol of diacid chloride gave white crystals that precipitated from the crude product mixture: yield 0.66 g, 16%; mp 143−145 °C (LB pet ether); IR (Nujol) 1760(s) and 1672(s) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 7.43 (m, 5H), 3.75 (s, 3H), 2.03 (q, 4H), 1.63 (q, 4H), 1.06 (t, 6H), and 0.47 (t, 6H); MS m/z (rel intensity) 260 (3) ($M - C_7H_{17}NO_3$), 247 (45), 246 (100), 219 (52), and 105 (99); HPLC purity (254 nm, Partisil 10, hexane/EtOAc (80:20): 99.6%.; HRMS m/z $[M - C_7H_{17}NO_3]^+$ calcd for $C_{15}H_{18}NO_3$ 260.1286, found 260.1286.

4,4-Dipropyl-2-(1-phenylethenyl)-3,5-isoxazolidinedione (8f). Reaction of 22 mmol of diacid chloride gave a colorless viscous liquid: yield 1.14 g, 18%; IR (neat) 1817, 1737 cm^{-1} (s); ^1H NMR (300 MHz; $CDCl_3$) δ 7.39 (s overlapping a small m, 5H), 5.56 (s, 1H), 5.44 (s, 1H), 1.87 (m, 4H), 1.40 (m, 4H), and 0.96 (t, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 13.9, 18.3, 38.1, 53.0, 109.1, 126.7, 128.5, 129.4, 133.1, 139.7, 169.0, 172.5; HRMS m/z $[M + H]^+$ calcd for $C_{17}H_{21}NO_3H$ 288.1601, found 288.1617; HRMS m/z $[M + Na]^+$ calcd for $C_{17}H_{21}NO_3Na$ 310.1420, found 310.1498.

***O,O′*-(2,2-Dipropyl-1,3-dioxo-1,3-propanediyl)-*E,E′*-dioxime 1-Phenylethanone (11f).** Reaction of 22 mmol of diacid chloride gave a white solid: yield 1.87 g, 40%; mp 104−105 °C (absolute EtOH); IR (Nujol) 1778, 1755 cm^{-1} (s); ^1H NMR (300 MHz; $CDCl_3$) δ 7.75 (m, 4H), 7.43 (m, 6H), 2.34 (s, 6H), 2.09 (m, 4H),

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1.40 (m, 4H), and 0.99 (t, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 14.4, 14.5, 17.5, 35.1, 57.2, 127.1, 128.6, 130.8, 134.5, 163.8, 168.5. Anal. Calcd for $C_{25}H_{30}N_2O_4$: C, 71.07; H, 7.14; N, 6.63. Found: C, 70.98; H, 7.14; N, 6.51.

2-(1-Cyclohexenyl)-4,4-diethyl-3,5-isoxazolidinedione (13a). Reaction of 20 mmol of diacid chloride gave 3.4 g of an unstable brown oil; yield 62%, initial yield gradually decomposed to 2% after 72 h by HPLC; ODS-2 using H_2O/MeCN (40:60) at 254 nm; IR(neat) 1817 (s), 1728 (s) cm^{-1}; ^{1}H NMR (60 MHz, $CDC1_3$) δ 5.96 (m, br, 1H)), 2.6 (m, 4H), 2.1−1.4 (m, 8H), and 0.90 (t, 6H).

1,l-Bis(2-(4,4-Diethyl-3,5-isoxazolidinedione)cyclohexane (14a). Reaction of 20 mmol of diacid chloride gave a white crystalline solid that precipitated over 72 h from the product mixture: yield 1.38 g, 35%; mp 102−103 °C (HB pet ether); IR (Nujol) 1810(s) and 1715 cm^{-1} (s); ^{1}H NMR (300 MHz; $CDC1_3$) δ 2.60 (br t, 4H), 1.86 (m, 8H), 1.69 (m, 4H), 1.57 (m, 2H), and 0.95 (t, 12H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 9.1, 22.3, 24.4, 28.7, 33.6, 54.5, 82.5, 70.2, 171.9; MS m/z (rel intensity) 238 (66%) (M − $C_7H_{10}NO_3$), 193 (10%), 164 (11%), 98 (26%), 97 (57%), 95 (100%). HRMS m/z [M − $C_7H_{10}NO_3$]$^+$ calcd for $C_{13}H_{20}NO_3$ 238.1443, found 238.1444. Anal. Calcd for $C_{20}H_{30}N_2O_6$: C, 60.89; H, 7.67. Found: C, 60.91; H, 7.62.

1,l-Bis(2-(4,4-Diethylisoxazolidine-3,5-dione)cyclopentane (14b). Reaction of 20 mmol of diacid chloride gave a white crystalline solid precipitated over 24 h from the crude product mixture: yield 0.62 g, 16%; mp 100−101 °C (LB pet ether); IR (Nujol) 1810 (s) and 1715 cm^{-1} (s); ^{1}H NMR (300 MHz; $CDC1_3$) δ 2.63 (m, 4H), 2.2−1.5 (m, 12H), and 0.95 (t, 12H). Anal. Calcd for $C_{19}H_{28}N_2O_6$: C, 59.98; H, 7.42; N, 7.37. Found: C, 59.75; H, 7.35; N, 7.29.

General Procedure for the Preparation of the 3-(1-Methylethenyl)-1*H*-2,3-benzoxazine-1,4(3*H*)-diones (16). In a three-neck flask fitted with an addition funnel and a condenser was prepared a solution containing acetone oxime (**7a**) (20 mmol) and Et_3N (60 mmol) in 70 mL of anhydrous Et_2O. The flask was swept with N_2, and the solution was chilled in an ice−water bath to 0 °C with stirring. To the cold solution was added dropwise over a 15 min period 20 mmol of the phthaloyl chloride (**15**) in 50 mL of anhydrous Et_2O. The solution was stirred at rt under N_2 for 24 h. The white precipitate was filtered, and the filtrate was washed with HCl (10%, 3 × 50 mL) and then dried ($MgSO_4$). The filtrate was concentrated to give crude **16**. Purification by column chromatography over silica gel gave pure **16**.

3-(1-Methylethenyl)-1*H*-2,3-benzoxazine-1,4(3*H*)-dione (16a). Reaction of 20 mmol of diacid chloride gave a white crystalline solid: yield 3.02 g, 74%; 60−200 mesh silica gel ($CHCl_3$); mp 102−103 °C; IR (Nujol) 1748, 1667 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.8−8.4 (m, 4H), 5.40 (s, 1 H), 5.18 (s, 1 H), 2.2 (s, 3H); HRMS m/z [M]$^+$ calcd for $C_{11}H_9NO_3$ 203.0582, found 203.0585. Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89. Found: C, 64.80; H, 4.62; N, 6.82. Compound **16a** gradually decomposed to **17a** over several months when stored in a capped vial at room temperature.

1*H*-2,3-Benzoxazine-1,4-dione (17a). Recrystallization of crude **11a** (see above) from cyclohexane and then $CHCl_3$ gave **17a** as a white crystalline solid: yield 0.37 g, 11%; mp 231−232 °C (lit. mp 226 °C[52]); IR (Nujol) 1760(s), 1685(m) cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.95 (m); HRMS m/z [M]$^+$ calcd for $C_8H_5NO_3$ 163.0269, found 163.0266. Anal. Calcd for $C_8H_5NO_3$: C, 58.89; H, 3.09; N, 8.59. Found: C, 58.89; H, 3.19; N, 8.45.

6- and 7-Methyl-3-(1-methylethenyl)-1*H*-2,3-benzoxazine-1,4(3*H*)-dione (16b) and (16c). Reaction of 20 mmol of diacid chloride gave a white crystalline solid: yield 3.78 g, 76%; 230−400 mesh silica gel (EtOAc/LB petroleum ether (5:95)); mp 70−110 °C; IR (Nujol) 1747, 1664 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.64−8.21 (m, 6H), 5.49 (s, 1 H), 5.48 (s, 1 H), 5.24 (s, 1 H), 5.23 (s, 1 H), 2.58 (s, 3H), 2.56 (s, 3H), 2.21 (s, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 19.8, 19.9, 22.1, 22.2, 112.4, 112.9, 121.1, 122.0, 128.2, 128.8, 129.6, 130.0, 130.2, 130.3, 135.0, 135.3, 140.0, 140.2, 147.5, 147.8, 156.2, 156.6, 159.9, 160.4; MS m/z (rel intensity) 217 (0.1), 173 (33), 55 (100). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.11; N, 6.45. Found: C, 66.13; H, 5.23; N, 6.33. The ^{1}H NMR peak integration ratio of the two methyl singlets at δ 2.58 and 2.56, respectively, was 58:42.

6- and 7-Methyl-1*H*-2,3-benzoxazine-1,4(3*H*)-dione (17b) and (17c). A mixture (52:48) of **16b** and **16c** weighing 1.91 g (8.8 mmol) was exposed to the atmosphere at rt for 2 weeks. Analysis of the solid by HPLC showed 33% decomposition of the alkene mixture, The solid was stirred in 20 mL of cold $CHCl_3$ for 15 min and filtered to yield a mixture of **17b** and **17c** as a white solid: yield 0.48 g, 31%; mp 188−194 °C dec ($CHCl_3$); IR (Nujol) 1759 (s), 1659 (s) cm^{-1}; ^{1}H NMR (300 MHz; acetone-d_6) δ 7.78−8.08 (m, 6H), 2.60 (d, 3H) and 2.58 (s, 3H); ^{13}C NMR (75 MHz; DMSO-d_6) δ 17.1, 17.4, 116.7, 119.1, 120.3, 121.4, 121.5, 122.8, 124.3, 124.6, 130.9, 132.5, 140.9, 142.9, 154.5, 154.6, 157.5, and 157.8. The peak integration ratio of the two ^{1}H NMR methyl singlets at δ 2.60 and 2.58, respectively, was 52:48. Anal. Calcd for $C_9H_7NO_3$: C, 61.01; H, 3.99; N, 7.91. Found: C, 60.74; H, 3.73; N, 7.68.

6- and 7-Methoxy-3-(1-methylethenyl)-1*H*-2,3-benzoxazine-1,4(3*H*)-dione (16d) and (16e). Reaction of 11 mmol of diacid chloride gave a white crystalline solid: yield 0.77 g, 30%; 100−200 mesh silica gel (CH_2Cl_2); mp 93−105 °C; IR (Nujol) 1747, 1656 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.20−8.13 (m, 6H), 5.39 (s, 1 H), 5.37 (s, 1 H), 5.13 (s, 1 H), 5.11 (s, 1 H), 3.89 (s, 3H), 3.87 (s, 3H), 2.12 (s, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 18.8, 18.9, 55.1, 55.2, 109.1, 110.2, 111.1, 111.4, 111.5, 114.9, 120.9, 122.0, 122.6, 124.3, 129.1, 130.7, 131.5, 138.8, 154.7, 154.9, 158.5, 158.9, 162.9, 164.6; MS m/z (rel intensity) 233 (0.3), 189 (39), 55 (100). The ^{1}H NMR peak integration ratio of the two methoxy singlets at δ 3.89 and 3.87, respectively, was 52:48. Anal. Calcd for $C_{12}H_{11}NO_4$: C, 61.60; H, 4.76; N, 6.01. Found: C, 61.56; H, 4.63; N, 5.64.

Reaction of 1,4-Butanedioyl Chloride (23) with Acetone Oxime (7a). A solution of 1.83 g (25 mmol of acetone oxime (**7a**) in 50 mL of anhydrous Et_2O was cooled to 0 °C with stirring. To the solution was added 5.1 g (50 mmol) of Et_3N in 40 mL of dry ether. A solution of 3.9 g (25 mmol) of 1,4-butanedioyl chloride (**23**) was added dropwise over 15 min with stirring. The mixture was stirred at rt for 24 h. The mixture was filtered, dried ($MgSO_4$), and concentrated under reduced pressure to give a tan solid. Chromatography over silica gel (60−200 mesh) with EtOAc (100%) yielded *O*,*O*′-(1,4-dioxo-1,4-butanediyl)dioxime 2-propanone (**24**) as a pale yellow oil that solidified on standing: yield 1.05 g (37%); mp 60−63 °C (CCl_4/HB petroleum ether (2:1)); IR (Nujol) 1765 (s) cm^{-1} (s); ^{1}H NMR (60 MHz, $CDC1_3$) δ 2.8 0 (s, 4H), 2.08 (s, 6H), 2.03 (s, 6H); HRMS m/z [M − C_3H_6NO]$^+$ calcd for $C_7H_{10}NO_3$ 156.0060, found 156.0060. Anal. Calcd for $C_{10}H_{16}N_2O_4$: C, 52.62; H, 7.07; N, 12.28. Found: C, 52.37; H, 7.35; N, 12.05.

Stability of 3-(1-Methylethenyl)-1*H*-2,3-benzoxazine-1,4-(3*H*)dione (16a). *Thermal Stability.* A 0.50 g portion of **15a** was heated under N_2 for 1 h at 130 °C to yield a mixture of **17a** (98%) and *N*-hydroxyphthalimide (**20**) (2%): mp 231−232 °C. Heating **15a** for 3 h at 130 °C yielded a mixture of **20** (99%) and **17a** (1%): mp 233−234 °C (dec). (lit. mp 232−133 °C[74])

In Absolute EtOH for 30 h. A solution of 0.20 g of **16a** in 15 mL of absolute EtOH/CH_2Cl_2 (80:20) was allowed to stand at rt for 30 h. The solution was concentrated to give unchanged **16a**.

In MeCN/Water (75:25) at rt. A 4.9 × 10^{-2} M solution containing 0.50 g of **16a** in 50 mL of MeCN/water (75:25) was stirred at rt for 1 h. The MeCN was removed under reduced pressure, and the aqueous solution was extracted with $CHCl_3$ (2 × 50 mL). The $CHCl_3$ washings were dried ($MgSO_4$) and concentrated to give unchanged **16a**. A separate reaction was carried out for 10 h under the same conditions to give a white fluffy solid: mp 101−105 °C. Analysis by HPLC showed 8% decomposition.

In Refluxing MeCN/Water (75:25). A 4.9 × 10^{-2} M solution containing 0.50 g of **16a** in 50 mL of MeCN/water (75:25) was heated at reflux for 1 h with stirring. Upon cooling to rt the MeCN was removed under reduced pressure, and the remaining aqueous solution was extracted with $CHCl_3$ (2 × 25 mL). The $CHCl_3$ washings were dried ($MgSO_4$) and concentrated to give a mixture containing **17a** (93%) and **20** (7%) as shown by HPLC analysis. A separate reaction was carried out under the same conditions for 10 h to give a mixture containing **17a** (7%) and **20** (89%).

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Stability of 3-(1-Methylethenyl)-1*H*-2,3-benzoxazine-1,4(3*H*)-diones (16a) in Refluxing MeCN/Water (70:30). General Procedure for the Determination of the Relative Stabilities of 16a and mixtures of 16b and 16c and 16d and 16e. A solution of 0.020 g (0.10 mmol) of 3-(1-methylethenyl)-2,3-benzoxazine-l,4-dione (**16a**) in 20 mL of MeCN/water (70:30) was heated under reflux for 90 m. A small aliquot was removed every 15 min and analyzed by reverse phase HPLC using a solvent system of MeCN/water (70:30), a flow rate of 2.0 mL/min, and a detector wavelength of 280 nm. The peak areas were corrected for the weight response factors of the components. In a similar manner the decomposition of **16a** in refluxing MeCN/water/chloroacetic acid (68:29:3) and in refluxing MeCN/water/pyridine (67:29:4) were carried out. Also studied in each of the three refluxing solvent systems were a mixture of **16b** and **16c** (58:42) and a mixture of **16d** and **16e** (52:48).

Analysis of the Gas Evolved during Thermal Decomposition of 3-(1-MethyletHenyl)-1*H*-2,3-benzoxazine-l,4(3*H*)-dione (16a). *Preparation of Mercuric Derivative.* A procedure similar to that of Johnson and McEwen was used.[57] An ethanolic solution of the gas evolved in the thermal decomposition of **16a** at 130 °C was treated with aqueous alkaline mercuric iodide with stirring for 10 m. The precipitate was removed by suction filtration to yield a yellow-green powder: mp 190−210 °C partial melting. Johnson and McEwen reported that dipropynyl mercury melted at 203−204 °C.[57]

FTIR Analysis of the Gas Evolved during Thermal Decomposition. The gas evolved during the thermal decomposition of **16a** at 130 °C was collected in an IR gas cell and sealed: FTIR 2932 (w), 1737 (m), 1441(w), and 1365 (w) cm^{-1}. The FTIR spectrum was identical with that obtained with vaporized acetone.

GC−MS Headspace Analysis of the Gas Evolved during Thermal Decomposition. A 250 mL three-neck round-bottom flask was charged with 0.30 g (1.5 mmol) of **16a**. The flask was purged with N_2 for 1 h. The pressure was reduced to 55 Torr, and the sealed flask was submerged in an oil bath heated to 125 °C. Gas was evolved over 30 min. The flask was allowed to cool, and a sample of the headspace gas was analyzed by GC−MS. The gas was found to contain 5% acetone plus atmospheric components.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra and kinetic plots. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rizydore@durhameagle.com.

Present Address

[†]Durham Eagle LLC, 2602 Oberlin Dr., Durham, NC 27705

Notes

The authors declare no competing financial interest.

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