

stored in 5 mL of each of the following: hexane, diethyl ether, methylene chloride, *n*-butylaldehyde, and parent olefin. The solutions were stored at room temperature for 5 weeks and then analyzed. Results of the analyses are given in Table II. The epoxides were analyzed by GLC using column A for analytical work and column C for preparative work. They were identified by comparing their GLC retention times and infrared and NMR spectra with those of the appropriate authentic compound. The authentic epoxides were synthesized by treating the corresponding olefin with *m*-chloroperbenzoic acid. Butyric acid was identified by comparing GLC, IR, and NMR data with those of commercially available authentic compound.

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**Registry No.** *trans*-2,5-Dimethyl-3-hexene, 692-70-6; *cis*-2,5-dimethyl-3-hexene, 10557-44-5; *trans*-3-hexene, 13269-52-8; *cis*-3-hexene, 7642-09-3; hexane, 110-54-3; diethyl ether, 60-29-7; dichloromethane, 75-09-2; butanal, 123-72-8.

## Reactions of Azodiones with Electron-Rich Alkenes. 1,2,4-Triazoline-3,5-diones and Vinyl Ethers

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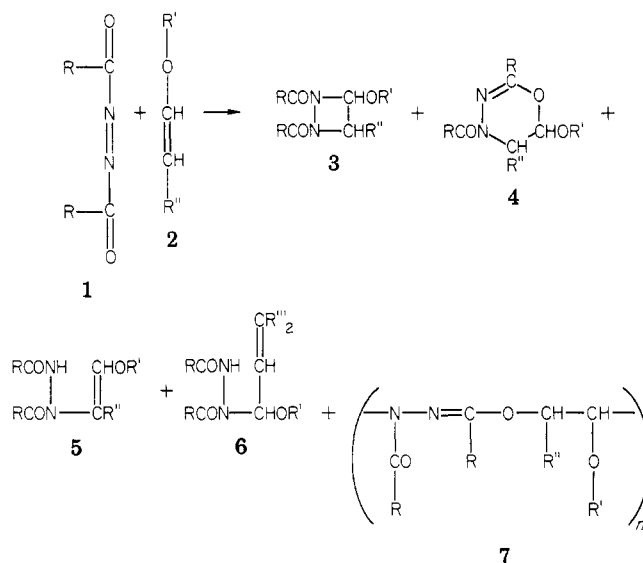
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4-Substituted-1,2,4-triazoline-3,5-diones (R-TAD) react with vinyl ethers to give mixtures of 1,2-diazetidines and polymers. The ratio of diazetidine to polymer is very dependent on the nature of the alkoxy substituent of the vinyl ether. For example, ethyl vinyl ether gives only polymer, but 2-chloroethyl vinyl ether gives only 1,2-diazetidines. The rate of reaction is very dependent on the vinyl ether structure, decreasing in the order  $\text{CH}_3\text{CH}_2\text{OCH}=\text{CH}_2 > \text{ClCH}_2\text{CH}_2\text{OCH}=\text{CH}_2 > \text{C}_6\text{H}_5\text{OCH}=\text{CH}_2$ , but is not very sensitive to the nature of the 4-substituent in the triazolinedione. The involvement of a 1,4-dipole in 1,2-diazetidines formation was proven by trapping the intermediate in the reaction of 2-chloroethyl vinyl ether and  $\text{C}_6\text{H}_5$ -TAD with acetone. However, the rate of the reaction is insensitive to the polarity of the solvent. In order to reconcile these facts, the initial formation of a charge-transfer complex is postulated, which in turn collapses to a 1,4-dipole.

The thermal reaction of conjugated azodiones (1) with electron-rich alkenes such as vinyl ethers (2) gives rise to a variety of products (Scheme I) including 2 + 2 cycloadducts (3), 2 + 4 cycloadducts (4), proton abstraction products (5), products of the ene reaction (6), and polymers (7).<sup>1-21</sup> The 2 + 4 cycloadduct (4) is usually the major product unless the alkene has allylic hydrogens; then ene

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Scheme I<sup>a</sup>



<sup>a</sup> R = alkyl, aryl, alkoxy, or -CONRCO-; R', R'' = H, aryl, alkyl.

product 6 formation becomes competitive with cyclization. However, in a few cases<sup>12</sup> 2 + 2 cycloaddition competes successfully with 2 + 4 cycloaddition. It has been postulated<sup>3-6,13-20</sup> that products 3, 5, and 7 arise from dipolar intermediates (8). The ene product cannot involve 8 and

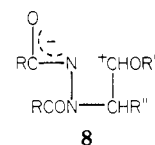
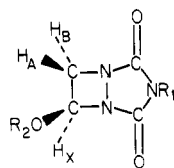


Table I. NMR Spectral Data for 1,2-Diazetidines<sup>a</sup>

R <sub>1</sub>	ref	R <sub>2</sub>	chem shift, ppm <sup>b</sup>			coupling const, Hz <sup>b</sup>		
			H <sub>A</sub>	H <sub>B</sub>	H <sub>X</sub>	J <sub>AB</sub>	J <sub>AX</sub>	J <sub>BX</sub>
C <sub>6</sub> H <sub>5</sub>		ClCH <sub>2</sub> CH <sub>2</sub>	4.68	4.34	5.27	9.94	5.75	4.12
C <sub>6</sub> H <sub>5</sub>		C <sub>6</sub> H <sub>5</sub>	4.89	4.54	6.50	10.00	6.77	4.58
CH <sub>3</sub>		C <sub>6</sub> H <sub>5</sub>	5.17	4.92	6.30	9.90	6.58	4.62
CH <sub>3</sub>		C <sub>6</sub> H <sub>5</sub>	4.53 (d)			6.01 (t)		
C <sub>6</sub> H <sub>5</sub>	3	CH <sub>2</sub> =CH	~4.5 (m)	5.9 (t)	or 6.6 (q)			
C <sub>6</sub> H <sub>5</sub>	4	(CH <sub>3</sub> ) <sub>3</sub> COCONH	4.7 (q)	3.6 (d)	5.9 (t)			
C <sub>6</sub> H <sub>5</sub>	5	C <sub>6</sub> H <sub>5</sub> CO	4.20 (m)			6.19 (m)		
C <sub>6</sub> H <sub>5</sub>	5	(CH <sub>3</sub> ) <sub>2</sub> CHCO	4.58 (q)	4.29 (q)	6.56 (q)	10	6	5
C <sub>6</sub> H <sub>5</sub>	5	(CH <sub>3</sub> ) <sub>3</sub> CO	4.60 (q)	4.27 (q)	6.49 (q)	10	6	5



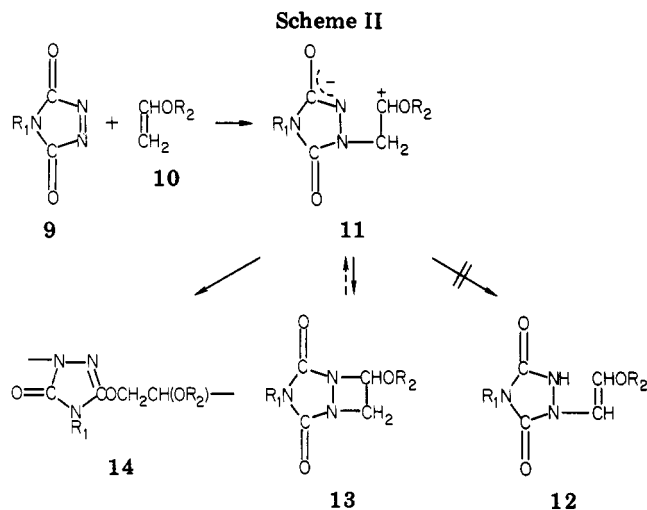
<sup>a</sup> The first three entries are in acetone-*d*<sub>6</sub>. The remainder are in chloroform-*d*<sub>1</sub>. <sup>b</sup> Parameters calculated by using LAOCOON (itrcal) for first three entries.

has generally been viewed as being formed via a concerted process;<sup>16-20</sup> however, more recent work has suggested that the reaction may involve formation of an aziridinium intermediate.<sup>29</sup> The 2 + 4 cycloadduct (4) could be formed from 8 or by a concerted Diels-Alder-type reaction.

In order to avoid the 2 + 4 cycloaddition and the ene reaction, we chose to look at the reaction of 4-substituted-1,2,4-triazoline-3,5-diones (R-TAD, 9) with vinyl ethers (10). It was hoped that by studying this system (Scheme II), it might be possible to reach some understanding as to the factors that determine whether the dipolar intermediate 11 undergoes proton transfer (12), 2 + 2 cycloaddition (13), or polymerization (14). It was hoped that this knowledge might give some clues as to why 1,2-diazetidines are formed in some reactions but not in others.

The first report of the 2 + 2 cycloaddition of R-TAD to olefins was by Gustorf,<sup>1</sup> who found that phenyl-TAD reacted with indene and with dihydro-1,4-dioxine to give 1,2-diazetidines. Hoffmann<sup>2</sup> reported 1,2-diazetidine formation in the reaction of phenyl-TAD with tetramethoxyallene. Butler and co-workers found that R-TAD forms diazetidines when reacted with divinyl ether<sup>3</sup> and with vinyl carbamates.<sup>4</sup> Vinyl esters react with R-TAD to give rearrangement products and polymer along with low yields of 1,2-diazetidines.<sup>5</sup> Guilbault<sup>9</sup> reported that 2,6-dichlorostyrene formed a diazetidine with phenyl-TAD as contrasted to styrene, which gave a 1:2 adduct. Rynbrandt<sup>10</sup> claimed diazetidine formation in the reaction of phenyl-TAD with an enamine but was unable to isolate the product. Phenyl-TAD also reacts with cyclopropyl-ethylene to give a 1,2-diazetidine.<sup>11</sup>

Butler et al.<sup>3</sup> reported that phenyl-TAD reacted with ethyl vinyl ether to give solely polymer (14). However, Wagener<sup>21</sup> later reported that when the reaction was carried out at -10 °C in an NMR tube, some 1,2-diazetidine was formed (4.65 (m, 1 H) and 5.80 ppm (t, 2 H) were reported, but these assignments are apparently reversed; see Table I). When the tube was warmed to +2 °C, these signals disappeared as polymer was formed over a 30-min period. In our work reaction of phenyl-TAD with *n*-butyl vinyl ether at 25 °C was examined briefly and found to give mostly polymer, but in one CCl<sub>4</sub>-soluble fraction, an ABX pattern was noted (X pattern, 6.38 ppm; AB pattern centered at 4.72 ppm), suggesting diazetidine formation. These observations suggest that diazetidine formation from the dipole may be a reversible process with simple alkyl vinyl ethers.



- a, R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>2</sub> = CH<sub>2</sub>CH<sub>2</sub>Cl  
 b, R<sub>1</sub> = CH<sub>3</sub>; R<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>  
 c, R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>

When 2-chloroethyl vinyl ether was reacted with phenyl-TAD in methylene chloride at room temperature, the diazetidine 13a was formed in quantitative yield (NMR). The solid was stable at room temperature for weeks in the absence of moisture. The proton NMR spectrum exhibited a clear ABX pattern. Similarly, phenyl vinyl ether was reacted with methyl-TAD and phenyl-TAD to give diazetidines 13b and 13c, which were isolated in 41% and 25% yields, respectively. In each of these cases, some polymer formation was noted. In the reaction of phenyl-TAD with 3,4-dihydro-2*H*-pyran only 1:1 polymer was formed, as shown by elemental analysis and the broad NMR lines at 1.8, 3.8, and 7.5 ppm.

In none of these reactions was it possible to detect the formation of H-transfer products 12. This was somewhat surprising in that such products are formed in the reaction of azo esters with ketene acetals,<sup>13</sup> and they are the only products formed in the reaction of phenyl-TAD with di-thioetene acetals.<sup>26</sup>

The NMR spectral data for 13c are given in Table I along with data published by Butler and co-workers.<sup>3-5</sup> As seen from the data in Table I, the appearance of the AB pattern of the diazetidine ring varies considerably. It was found that in acetone-*d*<sub>6</sub>, all 12 lines of the pattern were visible. However, in chloroform-*d*<sub>1</sub> the spectrum appeared

Table II. Effect of 2-Chloroethyl Vinyl Ether Concentration on Its Reaction with Phenyl-TAD<sup>a</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C

concn of 2-chloroethyl vinyl ether, M	10 <sup>2</sup> k <sub>2</sub> <sup>b</sup> , L mol <sup>-1</sup> s <sup>-1</sup>
0.100	13.9
0.200	11.1
0.400	12.8
0.500	12.6
	av 12.6 ± 0.7

<sup>a</sup> Initial concentration of phenyl-TAD = 0.0100 M.

<sup>b</sup> Calculated from the pseudo-first-order rate constant by dividing by the vinyl ether concentration.

Table III. Rate Constants and Activation Parameters for the Reaction of R<sub>1</sub>-TAD<sup>a</sup> and R<sub>2</sub>OCH=CH<sub>2</sub><sup>b</sup> in CH<sub>2</sub>Cl<sub>2</sub>

R <sub>1</sub>	R <sub>2</sub>	t, °C	10 <sup>2</sup> k <sub>2</sub> <sup>c</sup> , L mol <sup>-1</sup> s <sup>-1</sup>	ΔH*, kcal mol <sup>-1</sup>	ΔS*, eu
C <sub>6</sub> H <sub>5</sub>	ClCH <sub>2</sub> CH <sub>2</sub>	5.0	3.94 ± 0.35	7.7 ± 0.6	-36.9
		11.0	5.45 ± 0.30		
		25.0	11.9 ± 0.4		
		30.0	13.7 ± 1.0		
		36.0	18.6 ± 0.7		
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	7.0	1.1 ± 0.1	10.8 ± 1.6	-28.3
		28.0	4.83 ± 0.25		
		33.0	6.10 ± 0.85		
		40.0	10.0 ± 1.5		
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> ClCH <sub>2</sub> CH <sub>2</sub>	5.0	48.0 ± 9.5	9.6 ± 1.3	-32.2
		5.0	1.34 ± 0.10		
		22.0	3.86 ± 0.30		
		30.0	5.62 ± 0.10		
CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	5.0	11.11 ± 0.10	10.2 ± 1.9	-31.9
		22.0	1.44 ± 0.10		
		30.0	2.07 ± 0.10		
		38.0	4.18 ± 0.40		
CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	4.0	39.8 ± 0.2		

<sup>a</sup> Initial concentrations of RTAD = 0.0100 M. <sup>b</sup> Initial concentration of vinyl ether = 0.200 M. <sup>c</sup> k<sub>2</sub> calculated by dividing the pseudo-first-order rate constant by the vinyl ether concentration.

much simpler (see entry 3 and 4 in Table I). *N,N'*-Di-alkyl-1,2-diazetidines have highly puckered ring structures.<sup>22</sup> However, fusion to the urazole ring should tend to minimize the puckering, due to delocalization of the lone pairs on the nitrogens to the carbonyl groups. However, the values of *J*<sub>AX</sub> and *J*<sub>BX</sub> in Table I suggest some small puckering; i.e., *J*<sub>AX</sub> is a little small and *J*<sub>BX</sub> is a little too large for a completely planar structure.<sup>22</sup> With the assumption that the diazetidone ring is only slightly puckered, the larger *J*<sub>AX</sub> was assigned to the cis interaction and smaller *J*<sub>BX</sub> to the trans interaction. The changes in the spectrum with solvent may be due to changes in the coupling constants, caused by changes in solvation and puckering of the diazetidone ring.

In the course of this investigation, substantial differences in the rates of reaction of R-TAD's with vinyl ethers was noted. At room temperature alkyl vinyl ethers react with phenyl-TAD in a few seconds, chloroethyl vinyl ether in a few minutes, and phenyl vinyl ether in a few hours. A kinetic study was undertaken to quantify the information. The reactions were carried out under pseudo-first-order conditions in methylene chloride with a large excess of the vinyl ether. The rate was determined by following the disappearance of the R-TAD spectrophotometrically. The kinetic data are recorded in Tables II and III. As seen

Table IV. Solvent Effects on the Reaction of Phenyl-TAD with 2-Chloroethyl Vinyl Ether at 25 °C

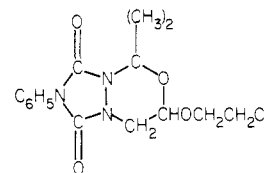
solvent	E <sub>T</sub> <sup>b</sup>	k <sub>2</sub> <sup>d</sup> , L mol <sup>-1</sup> s <sup>-1</sup>
benzene	34.5	0.27
bromobenzene	37.5	0.10
ethyl acetate	38.1	0.014
chloroform	39.1	0.18
methylene chloride	41.1	0.13
ethylene chloride	41.9	0.12
acetone	42.2	0.014
dimethyl sulfoxide	45	<0.15 <sup>c</sup>
acetonitrile	46.0	0.043
nitromethane	46.3	<0.11 <sup>c</sup>

<sup>a</sup> The initial concentration of 2-chloroethyl vinyl ether was 2.00 × 10<sup>-1</sup> M and of 4-phenyl-1,2-triazoline-3,5-dione was 1.00 × 10<sup>-2</sup> M. <sup>b</sup> Reference 25. <sup>c</sup> These are maximum values since phenyl-TAD slowly reacts with these solvents. <sup>d</sup> k<sub>2</sub> was calculated from the pseudo-first-order rate constant by dividing by the 2-chloroethyl vinyl ether concentration.

in Table II, the reactions are first order in both azo compound and vinyl ether.

The data in Table III show that the rate constants cover an overall range of ca. 10<sup>2</sup>. The relative rate of reaction of methyl-TAD with phenyl vinyl ether, 2-chloroethyl vinyl ether, and ethyl vinyl ether is in the ratio of 1:2.5:92. With phenyl-TAD the ratio is 1:2.5:30. The results clearly indicate a rather high sensitivity of the reaction to what are rather small electronic changes in the alkoxy group of the vinyl ether. This is exactly what would be expected if the reaction involved a 1,4-dipolar intermediate; i.e., the rate increases in the order C<sub>6</sub>H<sub>5</sub>O < ClCH<sub>2</sub>CH<sub>2</sub>O < CH<sub>3</sub>CH<sub>2</sub>O, which is the expected order for stabilization of the carbonium ion center of a 1,4-dipole. In addition to the data in Table III, it has been noted in related work<sup>23</sup> that 1,1-dimethoxyethylene reacts with phenyl-TAD within a few minutes at -78 °C, lending even stronger support to the concept of carbonium ion stabilization by the alkoxy groups. The sensitivity to substitution in the vinyl group was also mentioned by Butler and Wagener in the reaction of phenyl-TAD with vinyl esters.<sup>6</sup>

Turner et al. succeeded in trapping the 1,4-dipoles from phenyl-TAD and three alkyl vinyl ethers by carrying out the reaction in acetone or cyclohexanone.<sup>8</sup> We found that when phenyl-TAD was reacted with 2-chloroethyl vinyl ether in acetone, the 1,4-dipole could be trapped to give the tetrahydrooxadiazine 15 in 48% yield. Spectral evi-



15

dence was obtained suggesting the formation of a similar compound in the reaction of methyl-TAD with phenyl vinyl ether. When the diazetidone 13a was refluxed for 22 h in refluxing acetone, it was recovered unchanged, showing that 15 cannot be formed by reaction of 13a with acetone.

Huisgen and co-workers<sup>24</sup> noted a large solvent effect on the rate of reaction of tetracyanoethylene with vinyl ethers; i.e., the rate increased dramatically with increasing polarity of the solvent, consistent with 1,4-dipole forma-

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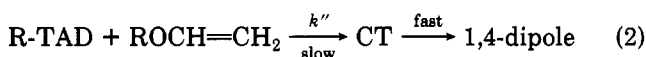
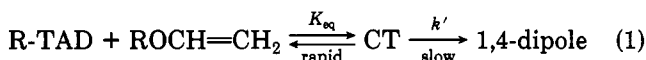
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tion. Similarly, it was anticipated that polar solvents would increase the rate of reaction of R-TAD's with vinyl ethers. In Table IV are listed the rate constants for the reaction of phenyl-TAD with 2-chloroethyl vinyl ether in ten different solvents. The rates vary only by a factor of 19 over the wide range of solvent polarities. In comparison with the  $E_T$  values,<sup>25</sup> it can be seen that there is no correlation at all between the rate of reaction and the polarity of the solvent. In fact the fastest rate is in benzene, the least polar solvent used.

At this point one must ask the question "how can a reaction that apparently involves formation of a 1,4-dipole and that is very sensitive to the effect of substituents in the vinyl ether not be affected by solvent polarity?" Perhaps the answer to this question is that formation of the 1,4-dipole is not the first step in the reaction. It would not be unreasonable to postulate the formation of a charge-transfer complex as the first step in the reaction, even though we have been unable to detect a charge-transfer (CT) band spectroscopically. Huisgen reported that vinyl ethers form charge-transfer complexes with tetracyanoethylene.<sup>24</sup> We have noted that R-TAD's form charge-transfer complexes with polyalkoxybenzenes and with 1-methylindole.<sup>26</sup>

The kinetic possibilities would be



In (1) the observed rate constant  $k_2 = k'K_{\text{eq}}$ . One would certainly expect  $k'$  to increase with increasing solvent polarity and stabilization of the carbonium center. In order to explain the lack of solvent effect, the equilibrium constant  $K_{\text{eq}}$  would have to decrease with increasing polarity. Since the starting materials are themselves quite polar, this may not be an unreasonable assumption.

Mechanism 2 is viewed as less likely in that it involves a rate-determining formation of a CT complex. In such a case the reaction might possibly be represented as an interaction of the LUMO of the R-TAD with the HOMO of the vinyl ether. The effect of substituents on the vinyl ether would affect the HOMO energy and hence the rate. At the same time, the polarity of the transition state, vis-à-vis the ground state, need not be affected appreciably by the vinyl ether substituent, and the rate could be independent of the polarity of the solvent.

Is it reasonable to expect that a CT complex could in fact open to a 1,4-dipole? The answer must of course depend on the structure of the CT complex; i.e., if its geometry allows facile formation of the C-N bond, it could indeed go directly to a 1,4-dipole.

In summary, our results suggest that the products of the reaction of R-TAD with vinyl ethers arise from 1,4-dipoles, which in turn arise from charge-transfer complexes. It should be emphasized however, that this result should not be general; i.e., if a charge-transfer complex does not have the right structure, it could be a dead-end path not leading to product.

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(26) Hall, J. H., unpublished results.

(27) STD-3G, MNDO and PRDDO all gave similar results. The squares of the coefficients for Phenyl-TAD from PRDDO are as follows:  $C_N^2 = 0.26$ ;  $C_C^2 = 0.12$ ;  $C_O^2 = 0.22$ . For methyl-TAD:  $C_N^2 = 0.27$ ;  $C_C^2 = 0.11$ ;  $C_O^2 = 0.21$ .

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## Experimental Section

All melting points are uncorrected. The IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer. The NMR spectra were recorded on a 90-MHz Perkin-Elmer R32 spectrometer. The coupling constants for ABX patterns were verified by using the LAOCOON program (itrcl) on a Nicolet Nic-1180 computer. The UV-vis spectra were recorded on either a Unicam Sp 800 or a Perkin-Elmer 340 spectrophotometer. The elemental analyses were performed by Gailbraith Laboratories Inc., Knoxville, TN.

4-R-1,2,4-Triazoline-3,5-diones were prepared by oxidation of the urazole with *N*-bromosuccinimide.<sup>30</sup> The vinyl ethers were purchased from Matheson, Coleman and Bell except for phenyl vinyl ether, which was purchased from Scientific Products, Inc. All vinyl ethers were distilled immediately before they were used.

**Reaction of R-TAD with Vinyl Ethers in Chlorinated Solvents.** The R-TAD (0.00229 mol) was dissolved in 20 mL of methylene chloride and this solution added to the vinyl ether (0.00229 mol) in 10 mL of methylene chloride. As soon as the red color had disappeared, the reaction was worked up as follows.

**(A) Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione with 2-Chloroethyl Vinyl Ether.** Concentration of the methylene chloride solution under vacuum gave white needles. The yellow solvent layer was decanted while still under vacuum to give a nearly quantitative yield of crude material, mp 125–131 °C. This compound is very moisture sensitive but is stable if stored in a desiccator. Repeated recrystallization gave an analytical sample: mp 131–132 °C; NMR <sup>1</sup>H (acetone-*d*<sub>6</sub>) δ 3.95 (4 H, m), 4.34 (H<sub>B</sub>), 4.68 (H<sub>A</sub>), 5.27 (H<sub>X</sub>), 7.51 (5 H, m).

Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>O<sub>3</sub>Cl: C, 51.16; H, 4.29; N, 14.91; Cl, 12.58. Found: C, 50.96; H, 4.44; N, 14.69; Cl, 12.72.

**(B) Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione with 3,4-Dihydro-2H-pyran.** Evaporation of the methylene chloride solution gave a white solid. It was transferred to a filter and washed with a minimum of cold methylene chloride to remove the slight yellow color. The yield of polymer was 90% (mp 155–163 °C). The NMR (acetone-*d*<sub>6</sub>) showed very broad peaks at δ 1.8 (5 H), 3.8 (4 H), and 7.5 (4 H), indicating polymer formation. The analysis indicated a 1:1 adduct.

Anal. Calcd for C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>: C, 60.22, H, 5.05, N, 16.21. Found: C, 60.18; H, 5.08; N, 16.14.

**(C) Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione with Phenyl Vinyl Ether.** Chloroform was used as the solvent instead of methylene chloride. Evaporation of the solvent gave a light yellow solid. This solid was washed several times with dry carbon tetrachloride to remove the yellow color to give a crude solid; mp 112–117 °C; yield 41%. This material absorbed moisture from the air rapidly and could not be purified further. The NMR indicated that the compound was essentially all 1,2-diazetidone: (acetone-*d*<sub>6</sub>) δ 3.00 (3 H, s), 4.92 (H<sub>B</sub>), 5.17 (H<sub>A</sub>), 6.30 (H<sub>X</sub>), 7.3 (5 H, m); (CDCl<sub>3</sub>) δ 3.12 (3 H, s), 4.53 (2 H, d), 6.01 (1 H, t), 7.3 (5 H, m).

**Reaction of R-TAD with Vinyl Ethers in Acetone.** The reactions were run in the same manner as described above for halogenated solvents.

**(A) Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione with 2-Chloroethyl Vinyl Ether.** After the red had disappeared, the acetone was removed. The residue was dissolved in methylene chloride (50 mL) and then poured into 300 mL of heptane. The precipitated material (mostly polymer) was filtered. The filtrate was concentrated to give crystals of **13a**: mp 117–118 °C; yield 48%; NMR (CDCl<sub>3</sub>) δ 1.73 (3 H, s), 1.85 (3 H, s), 3.7 (6 H, m), 5.07 (1 H, dd), 7.45 (5 H, m).

Anal. Calcd for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>Cl: C, 53.04; H, 5.34; N, 12.37; Cl, 10.44. Found: C, 53.06; H, 5.35; N, 12.23; Cl, 10.67.

**(B) Reaction of 4-Methyl-1,2,4-Triazoline-3,5-dione with Phenyl Vinyl Ether.** This reaction was carried out in acetone-*d*<sub>6</sub>. The NMR of the crude reaction contained, in addition to the peaks of the 1,2-diazetidone, peaks at (acetone-*d*<sub>6</sub>) δ 5.89 (1 H<sub>A</sub>, dd) and 3.82 (2 H<sub>AB</sub>, m), showing formation of a compound analogous to **15**. The compound could not be isolated.

**Kinetic Studies.** The rate studies reported in this paper were carried out under pseudo-first-order conditions, with a 20-fold

(30) Wamhoff, H.; Wald, K. *Org. Prep. Proc. Int.* 1975, 7, 251.

excess of the vinyl ether. The rate was followed spectrophotometrically by following the rate of disappearance of the colored R-TAD. The wavelength used varied from 526 to 544 nm ( $n \rightarrow \pi^*$ ) depending on the solvent.

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spectrometer used in the kinetic studies.

**Registry No.** 9a, 4233-33-4; 9b, 13274-43-6; 10 ( $R_2 = C_2H_5$ ), 109-92-2; 10a, 110-75-8; 10b, 766-94-9; 13a, 84559-65-9; 13b, 84559-66-0; 13c, 84559-67-1; 15, 84559-68-2; acetone, 67-64-1; 3,4-dihydro-2H-pyran, 110-87-2; 4-phenyl-1,2,4-triazoline-3,5-dione 3,4-dihydro-2H-pyran polymer, 84559-69-3.

## Metal Ion Oxidative Decarboxylations. 13.<sup>1</sup> Kinetics and Mechanisms of the Oxidation of *N*-Benzyliminodiacetic Acid with Cerium(IV) in Acidic Perchlorate and Acidic Sulfate Media<sup>2</sup>

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The Ce(IV)-mediated decarboxylation of *N*-benzyliminodiacetic acid (BIDA) produces benzaldehyde, formaldehyde, dimethylamine, benzylmethylamine, and *N*-benzylglycine in acidic perchlorate and acidic sulfate media. Spectrophotometric evidence of an intermediate Ce(IV)-BIDA complex is given. The data may be interpreted in terms of a mechanism which involves sequential reactions, the first of which is a reversible reaction: BIDA + Ce(IV) ( $k_1 \rightleftharpoons (k_{-1})$  complex ( $k_2$ )  $\rightarrow$  products. The rapid complex formation is followed by a slower oxidative decomposition to give a free radical capable of inducing free-radical polymerization. The free radical reacts rapidly with another Ce(IV) to give an iminium ion which undergoes either hydrolysis or decarboxylation. The rate constants  $k_1$ ,  $k_{-1}$ , and  $k_2$  were determined from kinetic data. At acidities between 0.10 and 2.0 M, the rates of both complex formation and complex decomposition are inversely dependent on  $[H^+]$ . Activation parameters were determined in perchloric acid. Evidence is given to suggest  $CeSO_4^{2+}$  as the reactive Ce(IV) species in acidic sulfate media.

In pursuing our studies of the oxidation and decarboxylation of hydroxy acids<sup>3</sup> and amino acids,<sup>4</sup> we have now chosen to investigate the mechanistic details of the cerium(IV)-mediated decarboxylation of *N*-benzyliminodiacetic acid (BIDA, 1). BIDA is a chelating agent which is used frequently, particularly in cross-linked polymer forms: Chelex 100 and Dowex A-1 ion-chelating resins. A knowledge of the compatibility of such agents with oxidizing metal ions prompted the present investigation. BIDA and the polymeric resins exhibit similar complexation behavior and are capable of forming 1:1 and 1:2 transition-metal complexes.<sup>5</sup> The thermodynamic properties of the resins can be identified with those of BIDA, and such information is useful in planning analytical separations with the ion-chelating resins.

In this paper we report the results of our investigation of the stoichiometry, products, kinetics, and mechanisms of the reaction of Ce(IV) with BIDA in acidic perchlorate and acidic sulfate media.

### Experimental Section

**Materials.** Cerium(IV) perchlorate solution (0.5 M in 6 M perchloric acid), ferrous ammonium sulfate (reagent ACS), 70%

perchloric acid (double distilled, reagent ACS), and sodium perchlorate (hydrated reagent) were obtained from G. Frederick Smith Chemical Co. *N*-Benzylglycine ethyl ester, *N*-benzyliminodiacetic acid (98%), benzylmethylamine (97%), dimethylamine (40% aqueous solution), and *N*-methylglycine (sarcosine, 98%) were obtained from Aldrich Chemical Co. Acrylamide, 5,5-dihydroxy-2,7-naphthalenedisulfonic acid (chromotropic acid; practical), and 2,4-dinitrofluorobenzene (2,4-DNFB) were from Eastman. Cerium(IV) sulfate (GR) and silica gel HF were from Merck. All other common reagents, indicators, and solvents were of the highest purity available from Fisher Scientific.

**Synthesis.** *N*-Benzylglycine, used as a standard for comparison, was prepared from *N*-benzylglycine ethyl ester through basic hydrolysis. The ethyl ester was heated with sodium hydroxide, poured over ice, and acidified with hydrochloric acid. White to off-white needlelike crystals formed immediately. The product was characterized by mass spectroscopy after recrystallization from water [mp 197 °C (lit.<sup>6</sup> mp 198–199 °C)].

**Solutions.** All solutions were made by using deionized water which was doubly distilled from an all-glass still. If the commercially available Ce(IV) perchlorate solution were found to contain polymeric cerium species,<sup>7</sup> it was first reduced with excess  $H_2O_2$  and reoxidized electrolytically as described previously.<sup>8</sup> If the test for polymeric species were negative, the Ce(IV) solution was simply diluted and standardized.

The solutions used for kinetic measurements were made just prior to use. The BIDA solutions contained known weights of BIDA and calculated quantities of stock solutions of perchloric acid and sodium perchlorate. For the experiments done in acidic sulfate media, the solutions were prepared as mentioned above except that known weights of  $Na_2SO_4$  were added just before the final dilution was made.

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(2) Results relating to portions of this work have been presented at the 5th IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, Aug 17–22, 1980, the 2nd Chemical Congress of the North American Continent, San Francisco, CA, National Meeting of the American Chemical Society, Las Vegas, NV, Aug 24–29, 1980, the 6th IUPAC Conference on Physical Organic Chemistry, Louvain-la-Neuve, July 11–16, 1982, Belgium, and ref 1.

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