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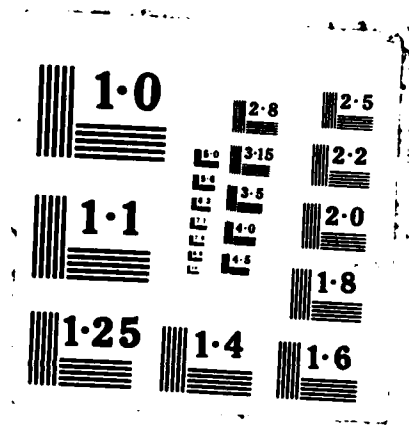
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SYNTHESIS AND CHARACTERIZATION OF 1,2-DISUBSTITUTED  
CYCLOBUTENE AMIDES: POLYMERS AND CYCLOADDUCTS

by

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A series of model diamides were synthesized from mono- and disubstituted amines with the diacid chloride of cyclobutene-1,2-dicarboxylic acid. Yields ranged from 30 to 70%. Melting points of the purified diamides ranged from less than 239°C for N-alkyl and N,N-dialkyl species to 204°C for the N-phenyl model. Relative rates of thermolysis (by DSC) with maxima from 208-224°C at 10°C/min. were dependent on the number and type of substituents, and intramolecular hydrogen bonding. Thermolysis products were Diels Alder dimers (for N-mono-substituted materials and for bulky tetrasubstituted models) while polymers formed spontaneously for two tetrasubstituted models with at least one methyl group on each nitrogen. Thermal imidization of cycloadducts was possible in some cases with concomitant oxidation to tetrasubstituted aromatic bisimides.			
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# SYNTHESIS AND CHARACTERIZATION OF 1,2-DISUBSTITUTED CYCLOBUTENE AMIDES: POLYMERS AND CYCLOADDUCTS

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## INTRODUCTION

2,3-Disubstituted cyclobutenes and their corresponding butadienes display a rich variety of addition reactions. The cyclobutenes can react via cycloaddition with appropriate dienes while the butadienes have been found to dimerize and polymerize as well as undergo typical [4 + 2] cycloadditions.

Recently, we reported the synthesis of diamides and polyamides based on cyclobutene-1,2-dicarboxylic acid to generate monomers and polymers with nascent butadiene functionality.<sup>1</sup> The cyclobutene moiety of such compounds generally undergoes thermal ring-opening above 180°C to form the corresponding 2,3-disubstituted butadiene.

We are currently exploring these compounds for synthesis of novel polybutadienes and for curing of thermosetting polymers and composites. Understanding the chemical behavior of the cyclobutene functionality in these systems is essential to evaluation of the composite cure process and final product performance.

We previously described our initial results on thermal reactions of some model diamides (1-3) and polyamides. Spontaneous polymerization occurred only for 2 while the others cyclodimerized. In an effort to better understand the factors controlling the spontaneous reactions of these butadienes, a number of additional derivatives (4-9) have been synthesized and their properties and behavior examined. We report here the general synthesis of these model compounds, their thermal reaction energetics, and their reaction products.

## EXPERIMENTAL

Facile synthesis of model amides was accomplished by reacting appropriate monofunctional amines with the intermediate cyclobutene-1,2-diacid chloride. The general synthesis was described previously<sup>1</sup> and extended to derivatives 4-7. <sup>13</sup>C NMR high-resolution and solid-state spectra were obtained on a Bruker MSL 200 spectrometer at a frequency of 50.32 MHz. Chemical shifts are reported in ppm from TMS (0 ppm). Thermal analysis was performed on a DuPont 910 Differential Scanning Calorimeter. Composition of the model compounds was confirmed by microanalysis (Desert Microanalysis, Tuscon, Arizona). Isolated yields, melting points, and <sup>13</sup>C NMR chemical shifts are given in Table 1.

## RESULTS AND DISCUSSION

### Thermal Analysis by DSC

DSC was used to investigate the onset and breadth of various thermally induced transitions and reactions, and to determine the enthalpy of the individual processes. Table 2 lists the values for melting points determined by DSC, the exotherm maxima (T<sub>max</sub>), and enthalpies for the peaks. For a given scan rate, the position of the maximum of a specific peak is an indication of the relative reaction rate.<sup>2</sup>

For the cyclobutene ring-opening process, T<sub>max</sub> varies less than 20°C for the series of derivatives 1-9. Cyclobutenes substituted in the 3-position, however, show a wide range of thermolysis rates that are strongly dependent on the type of

substituent.<sup>3</sup> Alkyl and aryl substituents on the amide nitrogen may be too far removed from the ring to exert more than nominal influence on ring-opening energetics.

The presence of intramolecular hydrogen bonding in the model amides, however, exerts a much stronger influence. Comparison of compounds 3-6 and 8 reveals almost identical T<sub>max</sub> independent of the R substituent. In the series, the relative rate of reaction decreases in the order N-alkyl > N-aryl > N,N-dialkyl > N-alkyl-N-aryl > N,N-diaryl. Hydrogen bonding increases the rate while aryl substituents decrease it.

Table 2. Thermal Analysis Results by DSC.

Cmpd	T <sub>m</sub> (°C)	T <sub>max</sub> (°C)	ΔH <sub>t</sub> (kcal/mole)
1	186.2	224.2	13.6
2	151.8	220.6	20.5
3	202.5	(211) <sup>a</sup>	----
4	72.0	208.3	11.4
5	56.4	208.2	23.2
6	--- <sup>b</sup>	208.2	17.4
7	--- <sup>b</sup>	214.5	24.6
8	156.0	208.2	14.7
9	183.6	228.4	21.4

<sup>a</sup>Peak obscured by melt endotherm

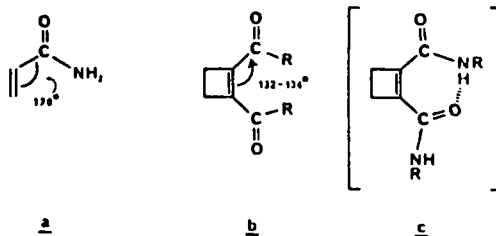
<sup>b</sup>Viscous oils at room temperature

The experimental heats of reaction (ΔH<sub>t</sub>) vary widely but do not appear to relate to the number or type of substituents. This probably results from the DSC exotherms being combinations of two or more reactions: ring-opening followed by either or both polymerization and cycloaddition. Indeed, compounds 4-6 show two overlapping exotherms clearly demonstrating the consecutive nature of these reactions. These three compounds undergo almost exclusive cycloaddition while 2 and 7 give only polymeric products. DSC scans of 2 and 7 show only one exotherm peak. The appearance of a single peak is not exclusive to polymer formation, however, since compound 1 shows only one peak yet undergoes only cycloaddition. The appearance of a bimodal exotherm, or lack of one, may simply be due to the difference in the rate of ring-opening and subsequent reactions.

### Polymerizability

The polymerizability of the butadiene compounds may be directly related to the occurrence of intramolecular hydrogen bonding in both the cyclobutene and the butadiene. Although the 7-membered cyclic structure required for the hydrogen bond in the former may at first appear strained, the large angle of the sp<sup>2</sup> hybridized carbons of the ring actually favor this structure (Figure 1a-c).<sup>4</sup>

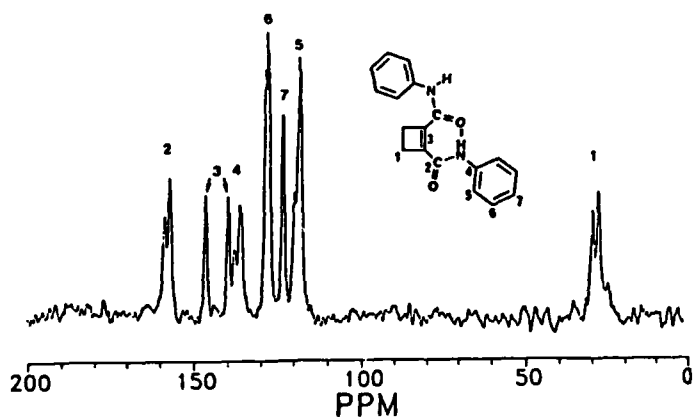
Figure 1



A similar structure has been confirmed by X-ray analysis of cyclobutene-1,2-dicarboxylic acid and invoked to explain its unusual cycloaddition behavior.<sup>5</sup> The solid state <sup>13</sup>C NMR of 3 is shown in Figure 2 along with the proposed intramolecular

hydrogen bonded structure. The large difference in alkene chemical shifts demonstrates a unique solid state interaction which may affect the ultimate reactivity of the model compounds and polyamides even in the melt and in solution.

Figure 2

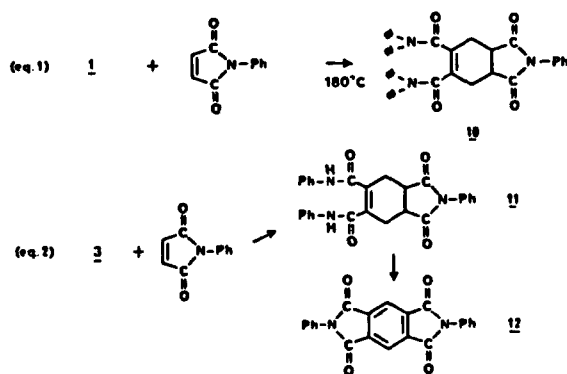


### Cycloaddition reactions

1,2-disubstituted cyclobutenes have been used to generate *in situ* substituted butadienes for Diels-Alder cycloadditions.<sup>6,7</sup> Cycloaddition offers another potential pathway for crosslinking of composite matrices. The model systems were studied to evaluate the facility of cycloaddition and the product formed.

The butadiene from 1 forms readily on thermolysis in bulk or in N-methylpyrrolidone. The diene did not polymerize, presumably due to the large steric bulk of the substituents, but slowly dimerized at 185°C. Cyclobutene 1 was also reacted with N-phenyl maleimide (nitrobenzene, 185°C, 6 h) to give the cycloadduct 10 (Figure 3, eq. 1) cleanly as evidenced by <sup>13</sup>C NMR.

Figure 3



Cycloaddition of N-phenyl maleimide with 3 resulted in formation of 11. Extended heating was found to convert 11 to 12, m.p. 452.5°C by DSC (lit. 453°C)<sup>8</sup> via aromatization of the cyclohexene ring and imidization (Figure 3, eq. 2). The final structure was confirmed by IR, solid state <sup>13</sup>C NMR, and microanalysis. The reaction scheme is further supported by the behavior of readily soluble (in DMSO and DMF) 11 which became insoluble on heating in air to give mainly 12.

### CONCLUSIONS

A series of model diamides was prepared from cyclobutene-1,2-diacid chloride and appropriate amines in good yields. The rate of ring-opening was found to be only marginally dependent on the

substituents. The general polymerizability of amide-substituted 1,3-dienes appears excellent. However, the fate of the generated butadiene (polymerization or cycloaddition) is highly substituent dependent, both hydrogen bonding and steric factors playing an important role. Finally, a novel synthesis of diimide 12 has been demonstrated which opens up a new synthetic approach to rigid rod polyimides involving soluble intermediates undergoing thermal cyclization and aromatization.

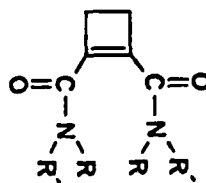
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\*in DMSO-d<sub>6</sub> rather than CDCl<sub>3</sub>.



1  
2  
3  
4  
5  
6  
7  
8  
9  
R  
phenyl  
methyl  
cyclohexyl

R  
phenyl  
phenyl  
n-dodecyl  
n-hexyl  
i-pentyl  
methyl  
cyclohexyl



Table 1. 1,2-Cyclobutenedicarboxylic Diamides Yields, Melting Points and <sup>13</sup>C NMR Characteristics.

Cmpd	Yd %	T <sub>m</sub> °C	1	2	3	Chemical Shift (ppm)	alkyl and aryl carbons
1	55	185-187	163.5	144.2	29.3	126-130	
2	63	150-152	163.9	143.5	29.3	126-131	
3*	68	202-204	159.9	144.7	25.5	137.5	128.3
4*	46	72-73	169.3	142.2			123.9
5	34	56-57	165.0	146.2	24.7	41.4	34.3
6*	45	oil	166	148.5	25	49	30.1
7	77	oil	163.5	139.5	28.4	36.3	33.8
8	40	155-160	161.1	143.7			29.0
9	32	159-162	164.8	136.5			27.2

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