The crude product was fractionated through a 4-in. Vigreux column. The first fraction was collected at water pump pressure (∼25 mm) and had bp 90–94 °C. This material was essentially pure 2,6-dimethylcyclohexanone (2.7 g). The product **2** was collected at 0.6 mm with bp 80–100 °C [lit.[5a] bp 82–100 °C (0.2 mm)] as a pale yellow oil (5.3 g, 51% yield at 71% conversion). The spectral properties of this material were identical with those reported previously for **2**.[5a]

***trans*-8,10-Dimethyl-1(9)-octal-2-one (1).** Diketone **2** was cyclized according to the procedure of Marshall and Schaeffer[5a] in sodium ethoxide/ethanol to give an 87% yield of distilled octalone (≥95% pure by VPC).

Acknowledgment. The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Vanderbilt University Research Council for their support of this work.

Registry No.—**1**, 17990-00-0; **2**, 4071-74-3; **4**, 4071-58-3; **5**, 1489-27-6; 2,6-dimethylcyclohexanone, 2816-57-1; methyl vinyl ketone, 78-94-4; 2-methylcyclohexanone, 583-60-8; cyclopentanone, 120-92-3.

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Conformational Equilibria in the *cis*-1,2,3,6-Tetrahydrophthalic Anhydride Series

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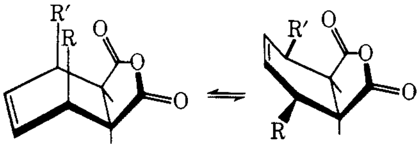
The use of lanthanide shift reagents (LSR) for conformational analysis can be approached in two ways. One method relates a ratio of proton slopes for the molecule being studied to the ratio of similar environmentally situated protons in skeletally homogeneous standards (the method of Servis and Bowler[2]). The second method utilizes the computer program PDIGM[3] to search for a conformer mix of lowest *R* values.[4] When suitable conformationally rigid molecules are available, the first method would appear to be more simple. This paper describes some of our work to test this assumption.

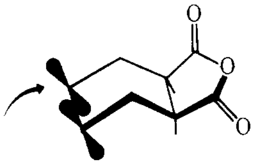
As part of our continuing program to evaluate how heteratoms can affect structure and reactivity of heterocyclic molecules,[5] we had the occasion to examine the anhydrides **1**,[6] **2**,[7] and **3**.[8] These can have, as seen by Dreiding models, two major contributing conformers which we designate as *"open"* and *"folded"*.



open *folded*

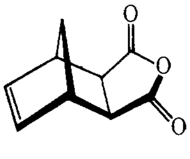
1, R = R′ = H
2, R = R′ = Me
3, R = H; R′ = Me

Epoxidation of **1** has been reported to give, as the major product, the epoxide syn to the anhydride moiety.[9] Although some participation of the anhydride functionality with the peroxy acid was not ruled out as a factor directing stereoselectivity, the major effect was thought to be conformational. In the *open* conformer, the steric effects are greater on the side of the π bond anti to the anhydride moiety.



Using NMR coupling constant data, however, **1** was determined to exist preferentially in the *folded* conformation.[10] Based primarily on the seemingly severe steric interactions of the methyl groups in the *open* conformation of **2**, this anhydride was also suggested to exist preferentially as a *folded* conformer. Anhydride **3** was also determined to be *folded*.

Since in our laboratories the anhydride functional group has been particularly well behaved toward LSR studies,[11] and because of the availability of **4** and **5** as models for the *open* and *folded* conformers, respectively, we chose to examine the conformer mix of **1**–**3** by the method of Servis. Additional representative *open* and *folded* models were available with **6**–**8**.[11]



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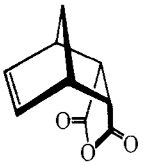

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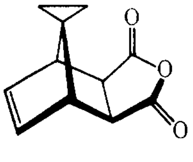

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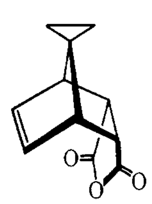

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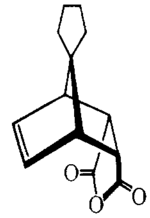

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To a weighed sample of the anhydride in deuteriochloroform was added Eu(fod)$_3$ in portions such that each spectrum constituted a 0.1 increment in the Eu(fod)$_3$ to substrate ratio. The chemical shifts for the vinyl and juncture protons (H_V and H_J, respectively) were obtained from the shifted spectra, and are listed in Table I.

In the experimental approach to this problem, we chose to compare the characteristic slope (*S*), obtained from a least-squares analysis of δ_{H_V} vs. ($\delta_{H_V} + \delta_{H_J}$) for each addition of shift reagent, where δ_{H_V} and δ_{H_J} are the chemical shifts for the vinyl and juncture protons, respectively. That the values for *S* do reflect the particular geometrical arrangement can be dramatically emphasized by comparing *S* values for the anhydrides **4**–**7** (Table I). Entries **4** and **6**, representative of *open* conformers, have very similar *S* values ($\bar{S}$ = 0.156 ± 0.002). Entries **5**, **7**, and **8** represent the *folded* conformer ($\bar{S}$ = 0.402 ± 0.004). Using the average values ($\bar{S}$) for the model compounds, 0.156 and 0.402 for 0.00 and 100% *folded*, respectively, we find that the three anhydrides do prefer the *folded* conformation: **1** (52%); **2** (71%); **3** (68%).

At this juncture it seemed appropriate to test the confor-

Table I. LSR Shift Data for Anhydrides

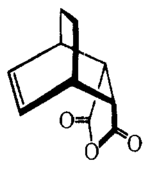
	Eu(fod)$_3$/substrate													
Compd	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	Hz	*S*	*r*
1	361	374	382	388	395	399	403	406	410	414	417	δ_{H_V}	0.288	0.999
	206	236	255	271	288	299	310	319	327	335	345	δ_{H_J}		
2	347	357	364	369	373	376	379	381	384	387	389	δ_{H_V}	0.331	0.999
	199	219	232	243	251	258	263	268	274	279	283	δ_{H_J}		
3	354	354	361	368	373	377	381	384	387	389		δ_{H_V}	0.324	0.999
	203	203	215	230	241	250	258	265	270	276		δ_{H_J}		
4	381	386	390	393	394	396	397	399	400	401	403	δ_{H_V}	0.154	0.996
	182	208	226	240	251	261	270	278	285	292	299	δ_{H_J}		
5	379	399	414	427	439	448	456	463	469	475	480	δ_{H_V}	0.401	1.000
	212	243	266	285	302	316	327	338	347	356	364	δ_{H_J}		
6	386	391	395	398	401	403	405	407	408	409	410	δ_{H_V}	0.157	0.995
	190	217	237	253	266	278	288	298	306	313	320	δ_{H_J}		
7	383	396	405	425	440	450	459	469	475	478	481	δ_{H_V}	0.399	0.999
	224	243	256	285	308	322	337	353	361	366	372	δ_{H_J}		
8	378	399	415	428	439	449	457	465	471	477	483	δ_{H_V}	0.406	1.000
	218	249	273	292	308	322	334	346	354	363	372	δ_{H_J}		
9	378	397	408	420	429	435	441					δ_{H_V}	0.362	0.999
	190	223	243	264	278	290	302					δ_{H_J}		

Table II. Conformer Mix–*R*-Value Relationships

Conformer mix (*folded* to *open*)	*R* value, %
1	
100:0	1.48
95:5	1.76
94:6	2.00
92:8	1.51
91:9	1.16
85:15	3.05
70:30	8.29
50:50	No minimum *R*
0:100	No minimum *R*
2	
100:0	7.36
97:3	4.33
95:5	2.67
91:9	0.86
90:10	11.33
50:50	12.06
0:100	No minimum *R*

mationally homogeneous models. Compound **9**[12] obviously fits the structural definition of a homogeneous *folded* molecule. The shift data are also recorded in Table I. From these data it would appear that **9** is only 83% *folded*. This clearly demonstrates that the constitution of the conformationally rigid models must be very similar to the compound being studied. In this case, simply changing the bridge size appreciably altered the characteristic slope values.

With the obvious problems associated with models which did not adequately resemble the molecules of interest, we next turned to PDIGM. Atom coordinates for the two conformers were obtained by combining x-ray data from **10**[13] and **11**,[14] for the cyclohexene and anhydride moieties, respectively.



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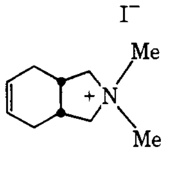

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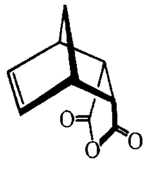

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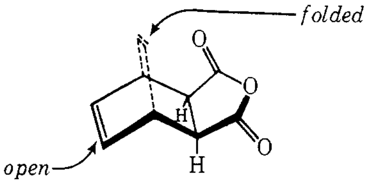
A minimum *R* value of 1.48% occurs at 2.90 Å when coordinates for the *folded* conformation are used as input for PDIGM. No acceptable minimum is reached when the *open* coordinates are used. Next we averaged different weights of the coordinates for the two conformational extremes, in order to determine the conformational mix. The method most acceptable to PDIGM involves arranging the two conformers as in **12**, in which the Lewis base sites take up the same coordinates positions. A weighted average of the two sets of coordinates is taken, and the resulting coordinate file is used for the PDIGM analysis.[15] The results of averaging **1** and **2** are given in Table II. A 91:9 (*folded:open*) mix of the conformers gives the lowest *R* value for both compounds. The lowest agreement factor for **1** is 1.16% and for **2** is 0.86%. These data are consistent with the preferred *folded* conformations suggested by the coupling constant results.



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From these results, the importance of good molecular coordinates is indicated[16] for conformational work by the PDIGM method. When these are available, the method appears very useful. However, it is obvious that the quantitative use of PDIGM for conformational analysis will be as dependent on accurate coordinate systems as the Servis method is dependent on proper models.

Experimental Section

The anhydrides have been previously prepared and references are provided in the text. Our samples were identified by physical and spectral data.

The NMR spectra were recorded on a Varian Model A-60 instrument, using tetramethylsilane as an internal standard. Weighed samples of Eu(fod)$_3$ were added to the anhydride dissolved in deuteriochloroform.

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Registry No.—**1**, 935-79-5; **2**, 36337-42-5; **3**, 35438-81-4; **4**, 2746-19-2; **5**, 129-64-6; **6**, 56587-29-2; **7**, 56587-27-0; **8**, 56587-28-1; **9**, 24327-08-0.

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(15) We have utilized coordinate averaging rather than shift averaging as a matter of manipulative convenience. A detailed comparison of these methods as well as a more complete description of the PDIGM procedure is contained in ref 5a. The number of different proton shifts utilized in the PDIGM calculation were **1**, 4; **2**, 4; **3**, 3; **4**, 5; **5**, 5; **6**, 5; **7**, 4; **8**, 4; **9**, 4.

(16) The sensitivity of the Servis method to proper models can readily be appreciated in the observation that **9** does not seem *folded* relative to the norbornyl models. That the PDIGM method could give results compatible with those from the Servis method was tested by compressing the computor coordinate system of the cyclohexene moiety of **1** so that the vinyl protons were closer to the anhydride ring (i.e., more resembling the norbornyl system). PDIGM found a minimum *R* of 2.16% at an 80:20 (*folded:open*) mix. Thus, we see that the PDIGM mix starts to approach that observed by the Servis method. And, because a reasonable minimum was found, the importance of good molecular coordinates in conformational work is indicated.

Micellar Effects on the Reaction of 2,4,6-Trinitrotoluene with Amines

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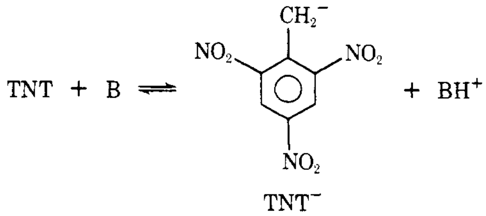
It is known that 2,4,6-trinitrotoluene (TNT) has a limited solubility (~5 × 10^{-4} M) in water at room temperature and produces a highly colored solution when reacted with strong bases.[1-6] The reaction has been interpreted as due to the formation of an intermediate, 2,4,6-trinitrobenzyl anion (TNT^-), which absorbs light in the visible region (at 500–525 nm).



TNT^-

In the presence of pyridine, TNT was found to react with benzaldehyde and 2,4,6-trinitrostilbene was produced. The intermediate was proposed to be TNT^-.[1]

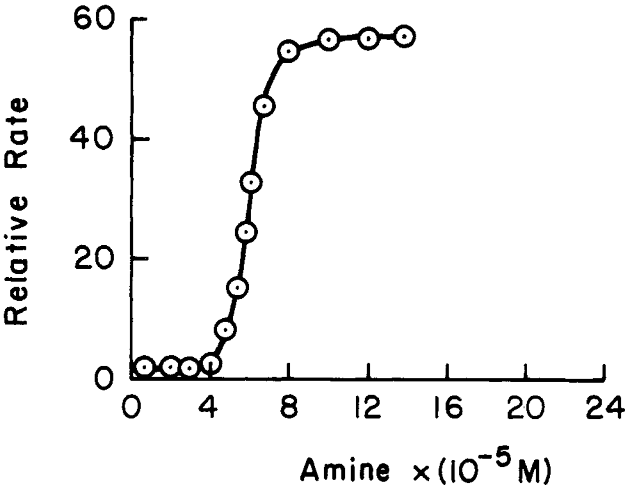


Figure 1. Relative rate of the formation of TNT^- vs. the concentrations of 4-dodecyldiethylenetriamine and 3,3′-diamino-*N*-methyldipropylamine at 25 °C in aqueous solutions. Initial concentration of TNT was 2.5 × 10^{-4} M.

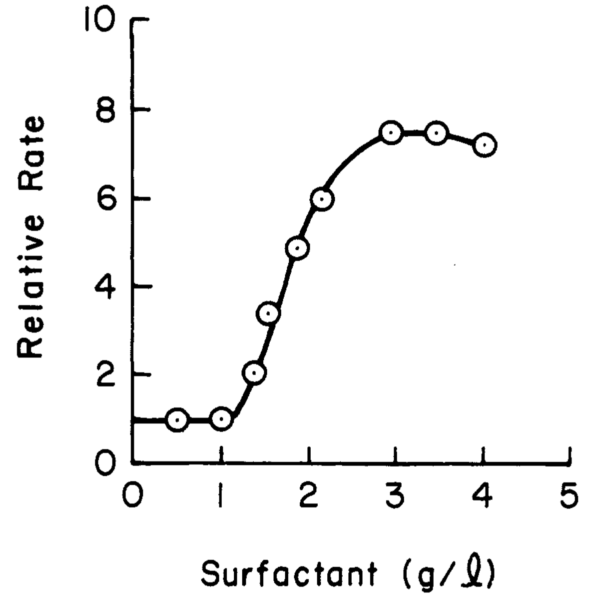


Figure 2. Relative rate for the formation of TNT^- in the reaction of TNT with II as a function of the concentration of alkylphenoxypolyethoxyethanol in aqueous solution at 25 °C. Initial concentrations of TNT and II were 2.5 × 10^{-4} and 1 × 10^{-3} M, respectively.

In the present work we investigated the reaction kinetics of TNT in aqueous solutions with two amines, i.e., 4-dodecyldiethylenetriamine (I), which is a surfactant, and a nonsurface-active triamine, 3,3′-diamino-*N*-methyldipropylamine (II). The results are shown in Figure 1. It was observed that I has a critical micelle concentration at about 5 × 10^{-5} M.[7] Below this concentration, the reaction rates of TNT with I and II were identical. However, above the critical micelle concentration of I, the reaction rate of TNT with I increases sharply and eventually levels off. The rate increase is about 55-fold compared to the same reaction of TNT with II and the enhancement is accounted for by the micellar effect.[8]

In order to study the micellar effect further, the reactions of TNT with II were explored in the presence of both nonionic and ionic surfactants. Surfactants used were alkylphenoxypolyethoxyethanol and hexadecyltrimethylammonium bromide. These results are summarized in Figures 2 and 3. The rates were found to be increased in the presence of both sur-