(**4**) was prepared by heating 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone (0.50 g, 1.2 mmol) and 1-phenyl-1-propyne (0.28 g, 2.4 mmol) under reflux until the purple color was discharged. The resulting brown liquid was cooled to room temperature and stirred with 10 mL of acetone. The white solid was removed by filtration, washed with acetone, and recrystallized from toluene–petroleum ether to yield white crystals of **4** (0.24 g, 39% yield, mp 217–219 °C). The ^{1}H NMR spectrum featured resonances at δ 1.90 (3 H, s, CH_3), 1.95 (3 H, s, CH_3), 1.98 (3 H, s, CH_3), and 6.5–7.3 (23 H, m, aromatic H). Anal. Calcd for $C_{39}H_{32}$: C, 93.56; H, 6.44. Found: C, 93.46; H, 6.73.

At −10 °C the aromatic methyl region of the NMR spectrum consisted of four resonances of essentially equal intensity at δ 1.94, 1.96, 1.97, and 1.99. The two central resonances were not resolved. The resonances broadened when the sample was warmed and coalesced pairwise as was observed for **3**. Line-shape analysis yielded the results reported in Table I.

1-Ethyl-3,4-bis(3-methylphenyl)-2,5,6-triphenylbenzene (**5**). A solution of 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone (1.0 g, 2.4 mmol) and a large excess of 1-phenyl-1-butyne in 5 mL of triglyme was refluxed for 2 h. After the solution had cooled, 40 mL of water and 10 mL of ethyl ether were added and the resulting precipitate was collected by filtration. Vacuum sublimation yielded white crystals (0.3 g, 22% yield, mp 248–250 °C). The ^{1}H NMR spectrum ($CDCl_3$) featured resonances at δ 0.72 (3 H, t, CH_2CH_3), 1.92 (3 H, s, CH_3), 1.96 (3 H, s, CH_3), 2.36 (2H, q, CH_2CH_3), and 6.5–7.3 (23 H, m, aromatic H). Anal. Calcd for $C_{40}H_{34}$: C, 93.34; H, 6.66. Found: C, 93.08; H, 6.68.

At −5 °C the ^{1}H NMR spectrum of the aromatic methyl region featured four resonances of approximately equal intensity at δ 1.91, 1.93, 1.95, and 1.97. Coalescence similar to that observed for **3** occurred when the sample was warmed. Line-shape analysis gave the results shown in Table I.

1-(1-Hydroxyethyl)-3,4-bis(3-methylphenyl)-2,5,6-triphenylbenzene (**6**) was prepared from 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone (0.50 g, 2.4 mmol) and 4-phenyl-3-butyn-2-ol (0.50 g, 3.4 mmol) by the procedures described above for **4**. The resulting product was chromatographed (silica gel, toluene) to yield 0.32 g of **6** (25% yield, mp 257–259 °C). The ^{1}H NMR spectrum showed resonances at δ 1.20 (3 H, d, $CHOHCH_3$), 1.95 (3 H, s, aromatic CH_3), 1.99 (3 H, s, aromatic CH_3), 4.87 (1 H, q, $CH(OH)CH_3$), and 6.5–7.4 (23 H, m, aromatic H). Anal. Calcd for $C_{40}H_{34}O$: C, 90.53; H, 6.46. Found: C, 90.51; H, 6.57.

At −20 °C the ^{1}H NMR spectrum of the aromatic methyl region featured four resonances of approximately equal intensity at δ 1.94, 1.96, 1.98, and 2.00 which coalesced at higher temperatures to two resonances. Line-shape analysis yielded the results reported in the text. Although **6** contains a chiral center, no additional resonances were observed in the aromatic methyl region of the ^{1}H NMR spectrum at low temperatures.

1,2-Bis(3-methylphenyl)-3,5,6-triphenyl-4-*tert*-butylbenzene (**7**). A mixture of 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone (1.0 g, 2.4 mmol) and 3,3-dimethyl-1-phenyl-1-butyne[21] (0.8 g, 5.4 mmol) was refluxed for a total of 56 h. The excess alkyne was removed by allowing it to condense on a cool stirring rod. After the mixture had cooled, 3 mL of acetone was added and the resulting crystals were separated by filtration and washed with acetone several times to yield very small brown crystals (0.4 g, 31% yield). A portion of the product was recrystallized from hexane–toluene (2:1) and then sublimed under vacuum [230 °C (0.1 torr)] twice to yield white crystals, mp 297–299 °C. The ^{1}H NMR spectrum featured resonances at δ 1.06 (9 H, s, C_4H_9), 1.96 (6 H, multiple resonances, aromatic CH_3), and 6.4–7.4 (23 H, m, aromatic H). Anal. Calcd for $C_{42}H_{38}$: C, 92.94; H, 7.06. Found: C, 92.60; H, 6.95.

At 40 °C the ^{1}H NMR spectrum in the aromatic methyl region featured four poorly resolved resonances at δ 1.95, 1.96, 1.97, and 1.99. Warming the sample caused pairwise coalescence of the resonances, and at 80 °C two sharp resonances were observed. Although line-shape analysis proved somewhat more difficult for this compound than for those mentioned above due to the extensive overlap of resonances in the low-temperature spectrum, a satisfactory analysis was performed and yielded $\Delta G^{\ddagger}_{293} = 18.7$ kcal/mol for isomerization.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **1**, 68977-55-9; **2**, 69010-11-3; **3**, 71885-65-9; **4**, 71885-66-0; **5**, 71885-67-1; **6**, 71885-68-2; **7**, 71885-69-3; 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone, 64897-54-7; 3-methyl-1-phenyl-1-butyne, 1612-03-9; 1-phenyl-1-propyne, 673-32-5; 1-phenyl-1-butyne, 622-76-4; 4-phenyl-3-butyn-2-ol, 5876-76-6; 3,3-dimethyl-1-phenyl-1-butyne, 4250-82-2.

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(21) Mortreux, A.; Blanchard, M. *Bull. Soc. Chim. Fr.* **1970**, 4035.

Stereochemistry of the Cyclobutane Dimers of *trans*-Cycloheptenones

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Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received July 20, 1979

Irradiation of the three isomeric benzocycloheptadienones **10**, **14**, and **15** produces in each case a trans intermediate which can be trapped by furan. In the absence of a trapping agent, cyclobutane dimers are formed whose stereochemistry, established mainly by X-ray diffraction on crystals, differs for each of the three substrates (**10** → **12**; **14** → **18**, **19**; **15** → **22**, **23**, **24**, **25**). The formation of head-to-tail dimers **23** and **25** is novel and argues against a diradical mechanism. Dimer stereochemistry corresponds to a ${}_{\pi}2_s + {}_{\pi}2_a$ ground state cycloaddition between two trans species for **10**, a trans + cis species for **14**, and both types for **15**. A rationale in terms of the most strained trans intermediate being the least selective for its reaction partner is proposed to explain the results.

trans-2-Cycloheptenone is formed when the cis isomer is irradiated.[1] It reacts rapidly with dienes[1] and with nucleophiles,[2] but in the absence of trapping agents such as these, it forms cyclobutane dimers. The detailed structure of these dimers, and the mechanism by which they are formed, is still not known. For example, do they result from the combination of two trans isomers or from the combination of a trans and a cis isomer?

The situation is similar with *trans*-2-cyclooctenone,[2b,3] although the structures of dimers obtained from certain

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(1) (a) Corey, E. J.; Tada, M.; LaMahieu, R.; Libit, L. *J. Am. Chem. Soc.* **1965**, *87*, 2051. (b) Eaton, P. E.; Lin, K. *Ibid.* **1965**, *87*, 2052.

(2) (a) Nozaki, H.; Kurita, M.; Noyori, R. *Tetrahedron Lett.* **1968**, 2025. (b) Noyori, R.; Kato, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1460.

(3) (a) Eaton, P. E.; Lin, K. *J. Am. Chem. Soc.* **1964**, *86*, 2087. (b) Noyori, R.; Watanabe, A.; Kato, M. *Tetrahedron Lett.* **1968**, 5443. (c) Miyamoto, N.; Isiyama, S.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1973**, *29*, 2365.

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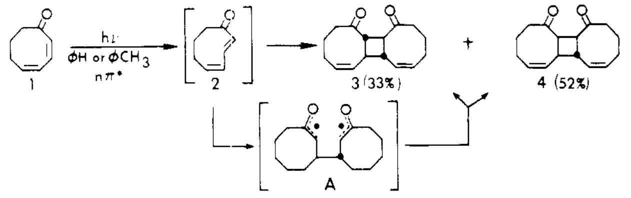
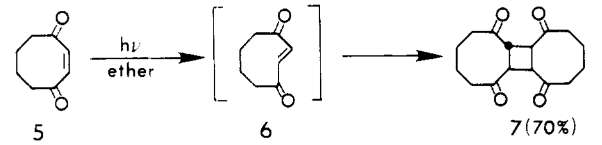
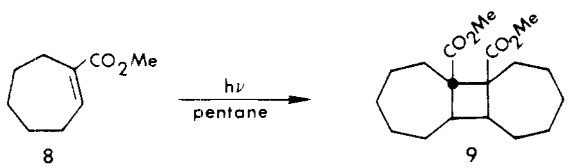
of its derivatives have been established. For example, 2,4-cyclooctadienone gives the two head-to-head dimers shown.[4] The authors suggested that the intermediate trans-dienone **2** dimerizes to biradical A which then closes in a con- or disrotatory manner to give the two observed dimers, but other mechanisms are possible (vide infra). A dimer with a stereochemistry similar to that of **4** was formed from the enedione **5**.[5] The authors suggest that

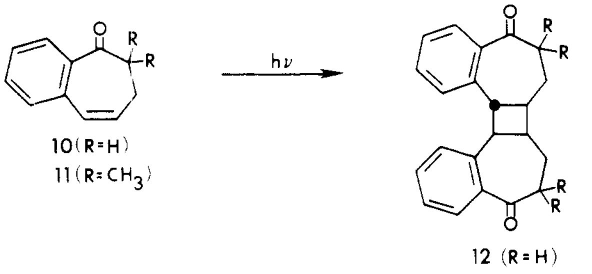




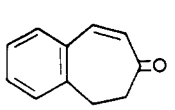
7 is formed from the allowed[6] $_{\pi}2_{\mathrm{s}} + {}_{\pi}2_{\mathrm{a}}$ thermal dimerization of the trans intermediate **6** (whose formation was demonstrated by trapping with dienes or a nucleophile). The same explanation could apply to the products from **1**, where **3** would arise from a trans + cis reaction (suprafacial for trans and antarafacial for cis) and **4** would arise from a trans + trans reaction.

Dimer stereochemistry similar to that of **4** and **7** has also been observed in several instances with seven-membered rings. For example, irradiation of the ester **8** in pentane gave dimer **9** as the major product.[7] The trans ester, presumed as the intermediate, could not, however, be trapped by furan or methanol. More pertinent to the present work is our previous report[8] that the principal cyclobutane dimers of **10** and **11** are **12** and **13**. In these cases, and also in the case of a naphtho analogue which gave similar dimers, the presence of the trans dienone as an intermediate was clearly established by trapping.

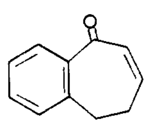




We now report on the photodimerization of **14** and **15**, analogues of **10** which differ only in the relative positions of the functionality. In **14**, the double bond and benzene ring are interchanged compared with **10**, whereas in **15** the system is cross-conjugated. We find that **10**, **14**, and **15** on irradiation all produce trans dienones which, however, give cyclobutane dimers with different stereochemical patterns. A possible explanation for the differences is offered.



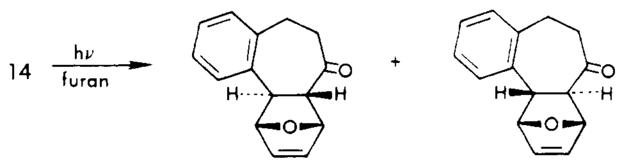
14



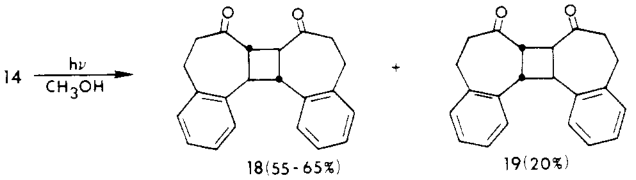
15

Results and Discussion

Irradiation of 14. Irradiation of a 0.05 M solution of **14** in furan, through a uranium glass filter, gave two crystalline adducts, **16** and **17**,[9] each of which had a trans ring fusion at the site of the cycloaddition. The stereochemistry of **16** and **17** was assigned from their NMR spectra (see Experimental Section). The photoproduct of **14** is thus established as the corresponding trans dienone.



Similar irradiation of **14** in methanol gave two cyclobutane dimers, **18** and **19**.[9] The major product (**18**) crystallized from solution during the irradiation. The structure of **18** was established by X-ray diffraction,[10] whereas the structure of **19** could be deduced from its NMR spectrum (vide infra). The same dimers were obtained when **14** was irradiated in acetic acid; in cyclohexane, the photolysis proceeded slowly but the major product (**18**) was isolated, together with recovered starting material.



Irradiation of 15. As reported previously,[11] irradiation of **15** in furan gave two trans cycloadducts, **20** and **21**.

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[4] Lange, G.; Neidert, E. *Can. J. Chem.* **1973**, *51*, 2207, 2215.

[5] Kayama, Y.; Oda, M.; Kitahora, Y. *Chem. Lett.* **1974**, 345.

[6] Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.

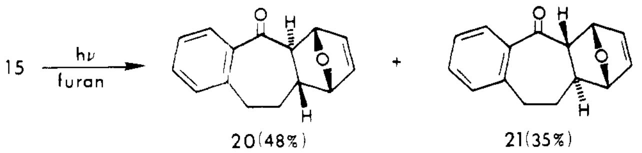
[7] Gibson, T. W.; Majeti, S.; Barnett, B. L. *Tetrahedron Lett.* **1976**, 4801.

[8] Dunkelblum, E.; Hart, H.; Suzuki, M. *J. Am. Chem. Soc.* **1977**, *99*, 5074.

[9] All yields are of isolated, pure crystalline product unless otherwise stated.

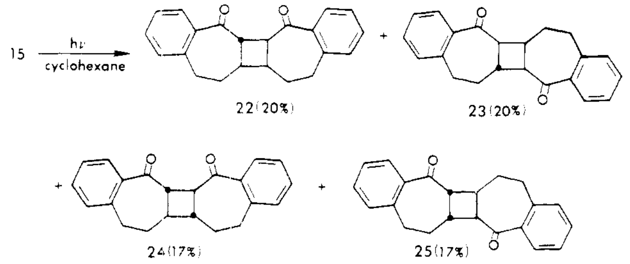
[10] Space group, cell parameters, and statistical data are as follows. **18**: space group *Pbcn* (No. 60); a = 10.883 (3) Å, b = 6.967 (2) Å, c = 21.852 (5) Å, $\alpha = \beta = \gamma = 90°$; R = 0.106 for 935 ($I > \sigma(I)$) data, R = 0.220 for all 1903 data, R_w = 0.064, goodness-of-fit = 1.204. All unique data were collected to 2θ = 55° with Mo Kα radiation. **22**: space group $P2_1/a$ (No. 14); a = 15.026 (2) Å, b = 10.276 (2) Å, c = 10.873 (3) Å, $\alpha = \gamma = 90°$, β = 108.59 (1)°; R = 0.049 for 2228 ($I > 2\sigma(I)$) data, R = 0.100 for all 3827 data, R_w = 0.041, goodness-of-fit = 1.287. All unique data were collected to 2θ = 55° with Mo Kα radiation. **23**: space group $P2_1/a$ (No. 14); a = 16.874 (3) Å, b = 7.708 (2) Å, c = 12.702 (2) Å, $\alpha = \gamma = 90°$, β = 95.24 (2)°; R = 0.083 for 1628 ($I > \sigma(I)$) data, R = 0.164 for all 2928 data, R_w = 0.051, goodness-of-fit = 1.004. All unique data were collected to 2θ = 50° with Mo Kα radiation. **24**: space group $P2_1/c$ (No. 14); a = 10.116 Å, b = 20.638 Å, c = 10.130 Å, $\alpha = \gamma = 90°$, β = 127.79°; R = 0.095 for 666 ($I > \sigma(I)$) data, R = 0.188 for all 1170 data, R_w = 0.072, goodness-of-fit = 1.226. All unique data were collected to 2θ = 35° with Mo Kα radiation. **25**: space group $P2_1/a$ (No. 14); a = 16.117 (3) Å, b = 9.267 (2) Å, c = 12.105 (3) Å, $\alpha = \gamma = 90°$, β = 114.75 (1)°; R = 0.078 for 1852 ($I > \sigma(I)$) data, R = 0.136 for all 2912 data, R_w = 0.055, goodness-of-fit = 1.209. All unique data were collected to 2θ = 50° with Mo Kα radiation. Positional and thermal parameters with standard deviations are available as supplementary material. Further details will be published elsewhere by Dr. Donald L. Ward.

[11] Hart, H.; Dunkelblum, E. *J. Am. Chem. Soc.* **1978**, *100*, 5141.

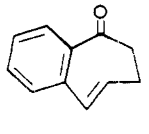


Consequently, as with **14**, the photoproduct is the corresponding trans dienone.

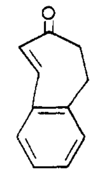
Irradiation of **15** in cyclohexane gave four crystalline dimers, **22–25**;[9] each structure was determined by X-ray diffraction.[10] Methanol could not be used as the solvent since it undergoes photoinduced Michael-type addition to **15**.[11] The formation of **23** and **25** constitutes the first example of head-to-tail dimerization in this type of reaction.



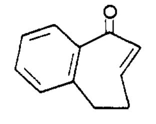
Mechanism. It is clear from the trapping experiments with furan that **10**, **14**, and **15** all produce a trans type of intermediate on irradiation. We will represent these intermediates as **10t**, **14t**, and **15t**, respectively, although



10t

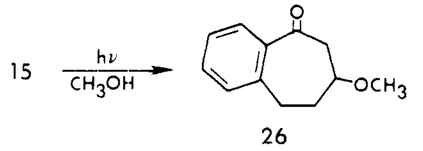


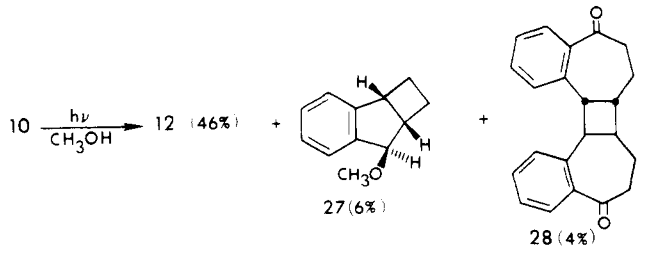
14t



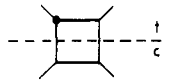
15t

these highly strained structures cannot be coplanar at the trans double bond. These intermediates, although they are all extremely strained, nevertheless show reactivity differences. Consider, for example, their behavior toward methanol. Irradiation of **15** in methanol gave only the methanol adduct **26**; no dimers were obtained.[11] On the other hand, **14** under identical conditions gave dimers (**18** and **19**) but no methanol adduct. And **10** behaved still differently, giving mainly dimer **12** but some transannular methanol adduct **27** and a small amount of another dimer, **28**.[8]





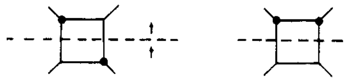
The main cyclobutane dimers from **10**, **14**, and **15** fall into two recognizable stereochemical patterns when viewed as products from ground state reactions of the trans intermediates operating under the restrictions of orbital symmetry conservation.[6] The most common pattern is shown by **10** (and **5**, **8**, and **11**), and results in a cyclobutane which is trans at one of the original double bonds and cis at the other:



If the reaction is a thermally allowed $_{\pi}2_s + {}_{\pi}2_a$ cycloaddition, then the only possibility (since at least one of the reactants must be trans) is that the product arises from the dimerization of two trans species.

Recent flash studies[12] on 2-cycloheptenone add support to this view of the reaction. By following the decay rate of *trans*-2-cycloheptenone as a function of initial enone concentration, it was shown that the rate constant for dimerization of two trans species is about 10^4 that of reaction between the trans and cis isomers. Thus even though the cis isomer is present in excess, dimerization can occur by the combination of two trans species.

The other extreme is represented by **14**, whose dimers correspond to either trans or cis geometry at both of the original double bonds:



If we again assume a $_{\pi}2_s + {}_{\pi}2_a$ cycloaddition, then both of these types of dimers arise from the reaction of the trans dienone with the cis isomer (either trans(s) + cis(a) or trans(a) + cis(s), respectively).

Dienone **15** gives dimers from both processes, in nearly equal amounts. Compounds **22** and **23** could arise from the combination of two trans isomers, whereas **24** and **25** could arise from trans + cis reactions.

The results can be rationalized with an additional assumption, viz., that the most stable, longest lived trans intermediate will be most selective in its reactivity and will give a dimer from a trans + trans reaction (i.e., the reaction with the larger rate constant). On the other hand, the least stable, shortest lived and most reactive trans intermediate will be less selective and react with the dienone present in greatest abundance, i.e., give a dimer from a trans + cis reaction.

If these assumptions hold, we would be obliged to conclude, from the observed dimer stereochemistry, that **14t** is the most strained and **10t** the least strained of the three trans intermediates. Is there any ground for these speculations? Yes, a little. The double bond in **14** lies between the carbonyl group and the aromatic ring. When it is twisted, virtually all conjugative stability is lost, whereas with **10t** and **15t**, some conjugation between the carbonyl group and aromatic ring remains.[13] Hence **14t** is expected to be the most reactive of the three isomers. The fact that **14t** could not be trapped by methanol is consistent with these arguments.

An a priori estimate of the relative strain in **10t** and **15t** is more difficult to make. That **15t** is fully trapped by methanol and **10t** is only trapped to a very limited extent might suggest that **10t** is more reactive than **15t**, whereas the dimer stereochemistry suggests the opposite order. Actually, the methanol comparison is probably misleading,

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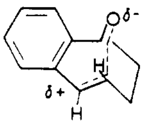
[12] Bonneau, R.; deViolet, P. F.; Joussot-Dubien, J. *Nouv. J. Chim.* 1977, *1*, 31.

[13] In *trans*-2-cycloheptenone, conjugation between C=C and C=O is negligible as shown by the change in $\nu_{C=O}$ from 1665 to 1715 cm^{-1} in going from the cis to the trans isomer.[1] Consequently **14t** will no doubt show less conjugative stabilization than either of its isomers.

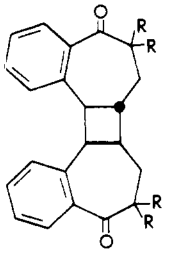
since **15t** is an α,β-enone and **10t**, a γ,δ-enone and hence less polarized. Indeed, in **10t** and its eight-membered homologue[14] the double bond is polarized in the reverse sense (C_γ is plus). To the extent that across-the-ring conjugation occurs, **10t** will be stabilized relative to **15t**. Clearly, some direct measurement of the lifetimes of these trans intermediates is necessary before one can conclusively demonstrate that the dimer stereochemistry and trans-monomer reactivity are related.



10t

Finally, the formation of **23** and **25** (head-to-tail dimers) from **15** tends to disfavor the diradical mechanism[4] for these dimerizations, since such a mechanism would require that 3,3′- and 2,3′-coupling occur with equal ease[15] whereas the former should be strongly preferred.

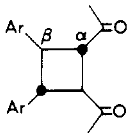
There is much that we do not yet understand about these dimerizations. That the reactions are under strict orbital symmetry control is apparent in all instances, but especially in the predominance of the all-trans dimer **18** from **14**. The preferred formation of **12** and **13** instead of their equally allowed counterparts **12′** and **13′** is probably the result of a steric effect, an effort to keep the aryl groups trans rather than cis. The formation of abnormal dimers rather than cyclobutane dimers when the carbon adjacent to the double bond is substituted with a *gem*-dimethyl group[8,16] can also be rationalized on steric grounds. Finally, it is not established that *all* of the dimers come from a trans precursor. Some, such as **19**, **25**, or **28**, could conceivably arise from a photochemical ${}_\pi2_s + {}_\pi2_s$ process; if operative at all, this reaction path can at best be a very minor process.



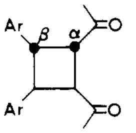
12′ (R=H)
13′ (R=CH$_3$)

NMR Spectrum and Structure of Dimer 19. Of the various dimers described in the Experimental Section of this paper, only that of **19** was not determined by an X-ray crystal structure. The reasons are that a suitable crystal was not available (**19** crystallized as needles); fortunately, the NMR spectrum showed that **19** had a symmetric structure which could be fairly safely assigned spectroscopically. When the NMR spectra of the dimers whose structures had been established by X-ray diffraction were determined in the presence of Eu(fod)$_3$, the head-to-head (h-h) dimers had slopes for the various peaks which were linear to about a 0.6–0.8 molar ratio of shift reagent to dimer; then they leveled off. For the head-to-tail (h-t) dimers (**23** and **25**), the slopes were linear to about a 1.3 molar ratio and then gradually leveled off. This suggested mainly 1:1 complexation for the h-h dimers, whereas for the h-t dimers each carbonyl group can complex separately with the shift reagent. Dimer **19** fell into the former, h-h pattern.

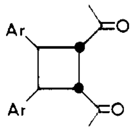
The 180-MHz NMR spectrum of **19** showed that the structure was symmetric, with a C_2 axis (essentially an AB pattern for the cyclobutane protons). The four h-h possibilities with this symmetry are



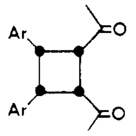
a



b



c



d

Of these, a has already been identifed as the major product of the reaction, **18**. The Eu(fod)$_3$ shift data strongly support arrangement b for the cyclobutane protons in **19**, since the slopes for the α and β protons (to the carbonyl groups) were virtually identical in both dimers (for **18**, α = 6.0, β = 3.0; for **19**, α = 5.7, β = 2.7). This would only be expected if the two carbonyl groups were similarly disposed in both dimers, and since they are known to be trans in **18**, we presume they are also trans in **19**. On these grounds we exclude arrangement c and the rather implausible d for the structure of **19**.

Experimental Section

General Procedures. NMR spectra were measured against Me$_4$Si as an internal standard on a Varian T-60 or HA-100 spectrometer or a Bruker WH180 spectrometer. IR spectra were calibrated against a polystyrene film and were recorded on a Unicam SP200 or a Perkin-Elmer 237 grating spectrometer. UV spectra were obtained on a Unicam SP-800 spectrometer. Mass spectra were obtained at 70 eV with a Hitachi Perkin-Elmer RMU-6 instrument. Melting points are uncorrected. Unless otherwise stated, column chromatography was performed with EM reagent silica gel 60, >230 mesh, with methylene chloride as the eluent. All irradiations were carried out with a Hanovia Type L 450-W lamp, under a N_2 atmosphere. Analyses were performed by Spang Microanalytical Laboratory and by Clark Microanalytical Laboratory.

4,5-Benzo-2,4-cycloheptadienone (14). 4,5-Benzotropone[17] (4.7 g, 30 mmol) in 150 mL of absolute ethanol was hydrogenated over 10% Pd/C at atmospheric pressure. After the uptake of approximately 1 mol equiv of H_2 (about 10 h) the crude mixture contained mainly the desired product and starting material (by NMR). Chromatography on 50 g of silica gel with CH_2Cl_2–hexane (2:3) gave 1.8 g (38%) of recovered 4,5-benzotropone and 2.5 g (85% based on consumed starting material) of **14** as an oil: IR (neat) $\nu_{C=O}$ 1660 cm^{-1}; NMR (CDCl$_3$) δ 2.60–3.10 (m, 4 H), 6.05 (d, 1 H, J = 12 Hz), 7.00 (d, 1 H, J = 12 Hz), 7.07–7.30 (m, 4 H); mass spectrum m/e (relative intensity) 158 (91), 130 (91), 129 (100), 128 (46), 115 (81). An analytical sample was collected by VPC (15% SE 30 on Chromosorb W, 6 ft × 0.25 in., 180 °C).[18]

Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.47; H, 6.37.

Irradiation of 14 in Furan. A solution of **14** (316 mg, 2 mmol) in 40 mL of furan was irradiated (uranium glass filter) for 3.5 h. The solvent was removed in vacuo and the residue was chromatographed on 75 g of silica gel with chloroform as the eluent (iodine detection) to give 105 mg (23%) of adduct **16**, mp 178–180 °C (recrystallized from hexane), and 160 mg (35%) of adduct **17**, mp 157–159 °C (recrystallized from hexane). **16**: IR (Nujol) $\nu_{C=O}$ 1710 cm^{-1}; mass spectrum m/e (relative intensity) 226 (1), 158 (88), 130 (75), 129 (35), 128 (24), 115 (35), 81 (100), 68 (17); NMR (CDCl$_3$)[19,20] δ 2.58 (d of d, 1 H, J = 7.5, 3 Hz, H$_1$), 2.74 (d, 1 H,

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(14) Suzuki, M.; Hart, H.; Dunkelblum, E.; Li, W. *J. Am. Chem. Soc.* **1977**, *99*, 5083.

(15) 3,3′-Coupling would lead to **22** + **24** (total yield 37%), whereas 2,3′-coupling would lead to **23** + **25** (total yield 37%).

(16) Hart, H.; Miyashi, T.; Buchanan, D. N.; Sasson, S. *J. Am. Chem. Soc.* **1974**, *96*, 4857.

(17) Thiele, J.; Schneider, J. *Justus Liebigs Ann. Chem.* **1909**, *369*, 287.

(18) Although pure by microanalysis, VPC showed that the sample contained 2% of 4,5-benzo-4-cycloheptenone.

J = 7.5 Hz, H_7), 2.40–3.00 (m, 4 H, $H_{3,4}$), 4.95 (br d, 1 H, J = 3 Hz, H_{11}), 5.24 (br s, 1 H, H_8), 6.45 (br s, 2 H, $H_{9,10}$), 7.00–7.32 (m, 4 H, aromatic). The relative Eu(fod)$_3$ slopes for H_1, H_7, H_8, and H_{11} were 1.6, 1.0, 2.1, and 1.7, respectively. **17**: IR (Nujol) $\nu_{C=O}$ 1715 cm^{-1}; mass spectrum *m/e* (relative intensity) 226 (1), 158 (83), 130 (100), 129 (64), 128 (38), 115 (62), 81 (49), 68 (37); NMR ($CDCl_3$)[19,20] δ 2.14 (d, 1 H, J = 8 Hz, H_1), 2.40–3.00 (m, 4 H, $H_{3,4}$), 3.25 (d of d, 1 H, J = 8, 3.5 Hz, H_7), 5.13 (br s, 1 H, H_{11}), 5.22 (d, 1 H, J = 3.5 Hz, H_8), 6.44 (br s, 2 H, $H_{9,10}$), 6.90–7.90 (m, 4 H, aromatic). The relative Eu(fod)$_3$ slopes for H_1, H_7, H_8, and H_{11} were 1.0, 1.3, 1.2, and 2.6, respectively.

Samples of **16** and **17** for analysis were prepared by sublimation at 150–160 °C (0.1 torr): **16**, mp 182–184 °C; **17**, mp 164–166 °C.

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found for **16**: C, 79.66; H, 6.18. Found for **17**: C, 79.75; H, 6.23.

Irradiation of 14 in Methanol. A solution of **14** (395 mg, 2.5 mmol) in 50 mL of methanol was irradiated (uranium glass filter) for 3 h. The major product crystallized from the solution as the photolysis proceeded. Filtration gave 218 mg (55%) of dimer **18**, mp 270–272 °C (in other runs, yields up to 65% were obtained). **18**: IR (Nujol) $\nu_{C=O}$ 1710 cm^{-1}; mass spectrum *m/e* (relative intensity) 316 (100), 171 (78), 158 (97), 130 (91), 129 (78), 128 (52), 115 (65); NMR ($CDCl_3$) δ 2.47–2.80 (m, 4 H, $C_{7,7'}$), 2.85–3.07 (m, 4 H, $C_{6,6'}$), 3.13–3.22 (d, 2 H, J = 7.2 Hz, with some additional splitting, $C_{2,2'}$), 3.53–3.6 (d, 2 H, J = 7.2 Hz, with some additional splitting, $C_{3,3'}$), 6.98–7.09 (m, 2 H, aromatic, ortho to cyclobutane ring), 7.11–7.30 (m, 6 H, remaining aromatic). Crystallization from ethyl acetate gave an analytical sample, mp 271–272 °C, and also a crystal suitable for X-ray diffraction.[22]

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.48; H, 6.29.

Evaporation of the solvent from the filtrate and chromatography of the residue on silica gel gave 80 mg (20%) of dimer **19** (needles from methanol, mp 268–269 °C). **19**: IR (Nujol) 1695, 1705 (sh) cm^{-1}; mass spectrum *m/e* (relative intensity) 316 (50), 171 (31), 158 (100), 130 (94), 129 (50), 128 (25), 115 (37); NMR ($CDCl_3$) δ 2.43–2.65 (sym m, 2 H), 2.75–2.92 (sym m, 4 H), 3.24–3.47 (m, 2 H), 4.32–4.57 (sym m, 4 H, appears mainly like two doublets, J = 11 Hz, further split (triplets?), $H_{2,2',3,3'}$), 7.06–7.26 (m, 8 H, aromatic). For further details of the NMR spectrum in the presence of Eu(fod)$_3$ shift reagent, see text.

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.48; H, 6.39.

Similar irradiation of **14** in acetic acid gave nearly the same yields of **18** and **19** in the same irradiation time as in methanol. Irradiation of **14** in cyclohexane gave, after 3 h, only a 13% yield of **18** and mainly recovered starting material.

Irradiation of 15 in Cyclohexane. A solution of **15**[11] (474 mg, 3 mmol) in 60 mL of cyclohexane was irradiated (uranium glass filter) for 7 h. Some precipitate formed during the irradiation. The solvent was removed and the products were isolated by one of two procedures.

Procedure A. Chromatography of the entire residue on 50 g of silica gel gave three main fractions. Fraction 1 (120 mg) was a heavy oil which slowly crystallized and was mainly **25** with some **23**. Fraction 2 (116 mg) was dimer **23**, mp 211–212 °C (acetone). Fraction 3 (201 mg) was a solid which contained mainly dimers **22** and **24**. Recrystallization from acetone gave 85 mg (18%) of pure **22**, mp 241–242 °C, and a little more of this product could be isolated from the mother liquors. However, attempts to obtain pure **24** from these solutions failed. To obtain pure **25**, the original chromatography was run with twice the amount of silica gel. Dimer **25** was obtained from the first fraction in 17% yield, mp 199–200 °C (acetone). This procedure, which involved prolonged chromatography, was advantageous for isolating pure **25**, the fastest moving dimer, but resulted in some decomposition of the other dimers.

Procedure B. The residue from an irradiation of **15** (395 mg, 2.5 mmol) was triturated with hexane and acetone; dimer **22** was soluble and could be isolated in 18% yield. The residue from the trituration was chromatographed on 100 g of silica gel. Dimer **24** was isolated in 18% yield, contaminated with traces of **22**. Crystallization was difficult and could not be prolonged, as it resulted in the transformation of **24** into another product. However, with care pure **24** could be obtained: mp 158–160 °C (methanol), mp 158–159 °C (acetone–pentane). The structures of **22–25** were determined by X-ray diffraction.[22]

22: IR (Nujol) $\nu_{C=O}$ 1680, 1668 cm^{-1}; mass spectrum *m/e* (relative intensity) 316 (40), 170 (100), 159 (42), 158 (64), 118 (68), 90 (87); NMR (60 MHz, $CDCl_3$)[23] δ 1.60–3.90 (m, 12 H), 7.05–7.40 (m, 7 H, aromatic), 8.00 (d of d, 1 H, J = 6, 2 Hz, aromatic); NMR (180 MHz, $CDCl_3$) δ 1.6–2.16 (m, 4 H, $H_{4,4'}$), 2.48 (quintet of d, 1 H, J = 9, 3.3 Hz, $H_{3'}$, long-range coupling to H_2), 2.6–2.8 (m, 1 H, H_3), 2.94 (d of d of d, 1 H, J = 14, 5.7, 2.0 Hz, $H_{5'}$ cis to H_2), 3.00–3.28 (m, 2 H, C_5 cis to H_2, $C_{5'}$ cis to $H_{2'}$), 3.38 (d of t, 1 H, J = 18, 3.7 Hz, H_5 trans to H_2), 3.65–3.80 (m, 2 H, $H_{2,2'}$), 7.16–7.50 (m, 7 H, aromatic), 8.08 (d of d, 1 H, J = 7, 3 Hz, H_8). In a Eu(fod)$_3$ study, protons H_2, $H_{2'}$, H_8, and $H_{8'}$ are the most shifted downfield; a plot of the shifts vs. mol equiv of shift reagent is linear to 0.6–0.8 mol equiv and then levels off. At 0.96 mol equiv (14 mg of **22** + 44 mg of Eu(fod)$_3$): δ 13.4 (d of d, 1 H, J = 8, 2 Hz, H_8), 13.15 (d of d, 1 H, J = 8, 3 Hz, $H_{8'}$), 11.4 (m, 1 H, H_2), 10.9 (d of d, 1 H, J = 12, 9 Hz, $H_{2'}$).

23: IR (Nujol) $\nu_{C=O}$ 1675 cm^{-1}; mass spectrum *m/e* (relative intensity) 316 (10), 159 (70), 158 (100), 157 (70), 90 (45); NMR (60 MHz, $CDCl_3$)[24] δ 1.50–3.20 (m, 12 H), 6.95–7.40 (m, 7 H, aromatic), 7.70–7.90 (m, 1 H, aromatic); NMR (180 MHz, $CDCl_3$) δ 1.60–1.94 (m, 2 H, H_4 syn to H_2, $H_{4'}$ anti to $H_{2'}$), 2.11–2.36 (m, 1 H, other H_4 or $H_{4'}$), 2.46 (d of m, *J*(*gem*) = 14 Hz, other $H_{4'}$ or H_4), 2.70–2.94 (m, 2 H, H_2 and $H_{3'}$), 2.94–3.32 (m, 6 H, remaining aliphatic protons), 7.06–7.46 (m, 7 H, aromatic), 7.82 (d of d, 1 H, J = 7, 2 Hz, H_8 or $H_{8'}$). In a Eu(fod)$_3$ study, only protons H_8 and $H_{8'}$ were clearly recognized. The shift plot was linear up to 1.3 mol equiv of shift reagent per mol of **23** and then leveled off.

24: IR (Nujol) $\nu_{C=O}$ 1680 (br) cm^{-1}; mass spectrum *m/e* (relative intensity) 316 (trace), 170 (65), 158 (82), 130 (100), 129 (75), 128 (50), 115 (80); NMR (60 MHz, $CDCl_3$)[23] δ 1.50–2.30 (m, 6 H), 2.70–3.40 (m, 6 H), 7.00–7.40 (m, 6 H, aromatic), 7.95–8.10 (m, 2 H, aromatic); NMR (180 MHz, $CDCl_3$) 1.50–1.80 (m, 2 H, $H_{3,3'}$), 1.90–2.16 (m, 4 H, $H_{4,4'}$), 2.84 (d of q, 2 H, $J_{2,3}$(trans) = 13.4 Hz and long range = 2.3 Hz, $H_{2,2'}$), 3.02–3.30 (m. 4 H, $H_{5,5'}$), 7.16–7.50 (m, 6 H, aromatic), 8.09 (d of d, 2 H, J = 7, 3 Hz, $H_{8,8'}$).

25: IR (Nujol) $\nu_{C=O}$ 1670 cm^{-1}; mass spectrum *m/e* (relative intensity) 316 (78), 170 (45), 158 (100); NMR (60 MHz, $CDCl_3$)[24] δ 1.65–2.40 (m, 5 H), 2.40–3.30 (m, 7 H), 6.95–7.45 (m, 7 H,

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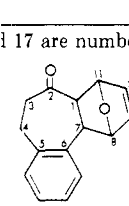
(19) Compounds 16 and 17 are numbered as follows:

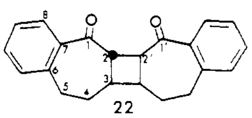


(20) It is known that in furan adducts of this type, only an exo proton (at C_1 or C_7) will couple with the adjacent bridgehead proton, since the dihedral angle between an endo and bridgehead proton is about 90°.[1b,8,11,21] In **16**, $J_{1,11}$ = 3 Hz and $J_{7,8} \simeq 0$, whereas in **17**, $J_{1,11} \simeq 0$ and $J_{7,8}$ = 3.5 Hz, fixing the relative stereochemistries in the two isomers. The coupling constants $J_{1,7}$ were 7.5 and 8.0 Hz in the two adducts, consistent with a trans ring fusion. H_1 appears at lower field in **16** than in **17**, whereas the reverse is true for H_7, consistent with deshielding of the exo proton in each case by the adjacent carbonyl group or aryl ring, as expected by examination of models. The low Eu(fod)$_3$ slope for H_1 and high slope for H_{11} in **17** (cf. **16**) also support the assigned structures. All chemical shift assignments were confirmed, where possible, by decoupling experiments.

(21) Anet, F. A. L. *Tetrahedron Lett.* **1962**, 1219. Fraser, R. P. *Can. J. Chem.* **1962**, *40*, 78.

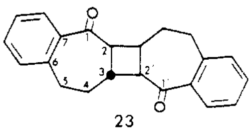
(22) Details will be published elsewhere by Dr. Donald M. Ward.

(23) The numbering used to describe the proton spectrum is



22

(24) The numbering used to describe the proton spectrum is



23

aromatic), 7.67–7.80 (m, 1 H, aromatic); NMR (180 MHz, $CDCl_3$) δ 1.80–2.04 (m, 2 H, $H_{4,4'}$ anti to $H_{3,3'}$), 2.06–2.26 (m, 2 H, $H_{4,4'}$ syn to $H_{3,3'}$), 3.10–3.30 (m, 6 H, $H_{2,2'}$, $H_{3,3'}$, $H_{5,5'}$ syn to $H_{3,3'}$), 3.40–3.64 (m, 2 H, $H_{5,5'}$ anti to $H_{3,3'}$), 7.14–7.36 (m, 6 H, arom), 7.46 (d of d, 2 H, J = 7, 2.5 Hz, $H_{8,8'}$).[25]

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found for **22**: C, 83.59; H, 6.43. Found for **23**: C, 83.48; H, 6.42. Found for **24**: C, 83.38; H, 6.38. Found for **25**: C, 83.60; H, 6.23.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE-05956) and the National Institutes of Health (Grant GM-15997) for financial support. We are also indebted to Dr. Donald L. Ward for the X-ray structure determinations.

Registry No. **14**, 69456-01-5; **15**, 45998-98-9; **16**, 71975-02-5; **17**, 72028-55-8; **18**, 71975-03-6; **19**, 72028-56-9; **22**, 72028-85-4; **23**, 71975-04-7; **24**, 71975-05-8; **25**, 71975-06-9; 4,5-benzotropone, 4443-91-8.

Supplementary Material Available: Positional and thermal parameters and their standard deviations for the X-ray structures of **18**, **22**, **23**, **24**, and **25** (9 pages). Ordering information is given on any current masthead page.

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[25] From the model of **25**, the carbonyl group is almost perpendicular to the aryl ring. Consequently $H_{8,8'}$ protons are at higher field than in the other three dimers. In **25**, $H_{5,5'}$ protons anti to $H_{3,3'}$ are equatorial and nearly in the plane of the aryl ring and consequently deshielded. The $H_{4,4'}$ protons anti to $H_{3,3'}$ are in pseudoaxial positions and are shielded by the carbonyl group.

Conformational Study of 3-Substituted Thietane 1-Oxides. Lanthanide Shift Reagent Approach

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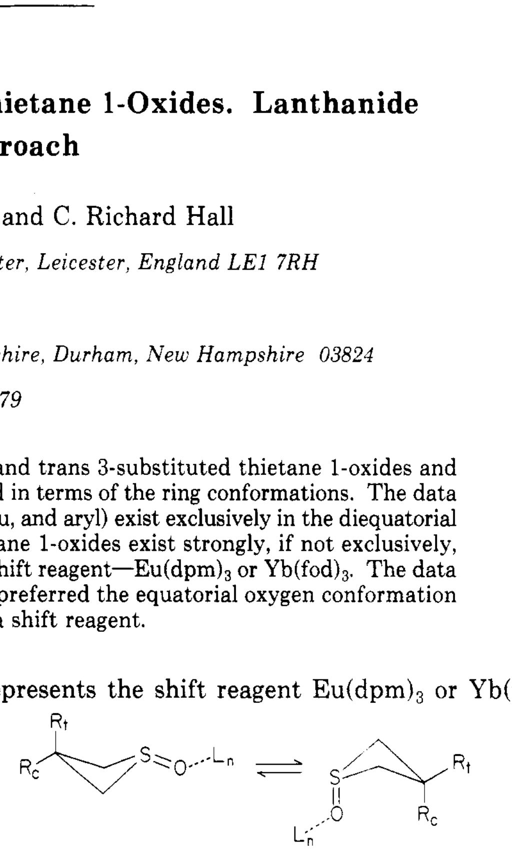
The NMR lanthanide-induced shifts (LIS) for a series of cis and trans 3-substituted thietane 1-oxides and 3,3-disubstituted thietane 1-oxides were measured and interpreted in terms of the ring conformations. The data suggested that all cis 3-substituted thietane 1-oxides (R = CH_3, *t*-Bu, and aryl) exist exclusively in the diequatorial conformation and that the two isomeric 3-methyl-3-phenylthietane 1-oxides exist strongly, if not exclusively, in the equatorial oxygen conformation when they are bound to a shift reagent—Eu(dpm)$_3$ or Yb(fod)$_3$. The data for trans 3-substituted thietane 1-oxides suggested that they all preferred the equatorial oxygen conformation (CH_3, 86%; aryl, 75%; *t*-Bu, 65–75%) when they are bound to a shift reagent.

Relatively little is known about the conformation of four-membered heterocycles such as thietane and its derivatives.[1] Pioneering work by Johnson[2] and co-workers showed that the sulfinyl group of 3-substituted thietane 1-oxides prefers to occupy the equatorial position. In his work 3-*tert*-butyl- and 3-arylthietane 1-oxides were equilibrated to mixtures which were rich (85%) in the cis isomer. Arguments based on the chemical shift of H(3) were presented which suggested that the cis isomers were mainly in the diequatorial conformation and that the trans isomers were mainly in the equatorial R/axial O conformation. More recently one of us (D.J.H.S.) presented proton NMR and X-ray evidence which questioned the latter suggestion.[3] Thus there is some uncertainty about whether the sulfinyl group prefers the equatorial position more than 3-aryl and 3-alkyl substituents.

Results and Discussion

In this paper we shall discuss lanthanide-induced shift (LIS) data for a series of thietane 1-oxides (**1**–**11**) in terms of the conformational equilibrium shown in eq 1, where Ln represents the shift reagent Eu(dpm)$_3$ or Yb(fod)$_3$.



(1)

I II

Chloroform solutions of the sulfoxides were doped with increasing amounts of Eu(dpm)$_3$ or Yb(fod)$_3$, and the proton (and in some cases carbon) NMR spectra were recorded as a function of shift reagent concentration. From these data the relative LIS for most protons (and carbons) could be determined (Table I). Previous work[4] has shown that the shift reagent coordinates with the sulfoxide oxygen. If the location of the shift reagent relative to the sulfoxide is known, then it should be possible to calculate the relative LIS for comparison with the experimentally determined ones. Good agreement implies that the shift reagent has been properly located, that the substrate's structure is correct, and that the NMR spectrum is properly assigned.[5] In our study we have assumed that all the thietane 1-oxides have the same shape, namely that reported for thiethane 1-oxide (**14**).[6] This is probably a good

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[1] For a review see: Moriarty, R. M. *Top. Stereochem.* **1974**, *8*, 271–421.

[2] (a) Johnson, C. R.; Siegl, W. O. *J. Am. Chem. Soc.* **1969**, *91*, 2796. (b) *Tetrahedron Lett.* **1969**, 1879. (c) Siegl, W. O.; Johnson, C. R. *Tetrahedron* **1971**, *27*, 341. (d) *J. Org. Chem.* **1970**, *35*, 3657.

[3] Barlow, J. H.; Hall, C. R.; Russell, D. R.; Smith, D. J. H. *J. Chem. Soc., Chem. Commun.* **1975**, 133.

[4] (a) Uebel, J. J.; Wing, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8910. (b) Wing, R. M.; Uebel, J. J.; Andersen, K. K. *Ibid.* **1973**, *95*, 6046.

[5] For a review of the lanthanide-induced-shift technique and its application in conformational analysis see: Hofer, O. *Top. Stereochem.* **1976**, *9*, 111–97.

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