was evaporated at the water pump to dryness from a 60° water bath and the residue distilled again to dryness twice after adding each time 25 ml of H_2O in order to complete the removal of acetic acid. The residue dissolved mostly at room temperature in 50 ml of 2 *N* hydrochloric acid. Again, insoluble neutral products were filtered, and the filtrate was oversaturated with concentrated ammonia, whereupon a crystalline precipitate of **9** (542 mg, 76%) was obtained. After repeated recrystallizations from ligroin slightly yellowish compact prisms, mp 182–183°, were obtained.

Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.14; H, 8.27; N, 9.58; mol wt, 292. Found: C, 81.95; H, 8.25; N, 9.38; mol wt, 291 (osmometric, acetone).

Mesitildiimine was also obtained in 66% yield from mesitildioxime (**11**) by the same procedure. The reduction of dimesitylfurazan oxide with sodium and ethanol gave **9** in 59% yield. Compound **4** was not affected by tin(II) chloride in boiling methanol or by heating with an excess of tri-*n*-butylphosphine for 3 hr to 140°.

Heating **9** (148 mg) with acetic anhydride (4 ml) for 4 hr to 100° yielded on cooling N,N′-diacetylmesitilidiimine (148 mg, 78%). After recrystallization from methanol, pale yellow needles, mp 264°, were obtained.

Anal. Calcd for $C_{24}H_{28}N_2O_2$: C, 76.56; H, 7.50; N, 7.44; mol wt, 376. Found: C, 76.27; H, 7.67; N, 7.26; mol wt, 379 (osmometric, chloroform).

N,N′-Dibenzoylmesitildiimine was obtained in 36% yield by benzoylation of **9** with benzoyl chloride and pyridine in the usual manner. After crystallization from ether, it melted at 247°.

Anal. Calcd for $C_{34}H_{32}N_2O_2$: C, 81.57; H, 6.44. Found: C, 81.74; H, 6.59.

Hydrolysis of Mesitildiimine.—Mesitildiimine (0.3 g) was heated on the steam bath for 3 hr with 30 ml of 2 *N* sulfuric acid whereby a yellow solid precipitated gradually from the solution. After cooling, the formed product was filtered and washed with water (0.25 g, 85%). One recrystallization yielded pure mesitil (**10**), mp 122°, identical with an authentic specimen.[9] Compound **10** was further characterized by oxidation with sodium peroxide to mesitoic acid according to the procedure given in the literature.[10]

Mesitildioxime (**11**).—A solution of mesitylmagnesium bromide was prepared from bromomesitylene (80 g), ethylene bromide (40 g), and magnesium turnings (17.5 g) in tetrahydrofuran (100 ml). To avoid precipitation of the Grignard compound 150 ml of tetrahydrofuran was added on completion of the reaction. With ice cooling, a solution of dichloroglyoxime (16 g) in tetrahydrofuran (150 ml) was then added dropwise within 2 hr. After the reaction mixture was left overnight at 25°, 300 ml of the solvent were removed by distillation and the residue was decomposed with ice and saturated ammonium chloride solution. The precipitated **11** was filtered off and was washed thoroughly with dilute hydrochloric acid and H_2O. The dioxime has a strong tendency to adsorb inorganic salts. The crude **11** (22 g, 70%) was recrystallized from dioxane or, preferably, acetic acid, mp 310° dec. A dioxime of structure **11** can occur in several stereoisomers; it has not been ascertained whether this material was uniform in this respect.

Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 73.96; H, 7.60; N, 8.42.

Dimesitylfurazan Oxide from Mesitildioxime.—Mesitildioxime (3.2 g) was dissolved in warm pyridine (100 ml) and 1 *N* sodium hydroxide (100 ml). Water (50 ml) was added, and the solution, which must remain clear, cooled quickly to 5°. Within 30 min, a cold solution of 1.6 g of bromine in 100 ml of 2 *N* sodium hydroxide was added with stirring. After 2 hr, the precipitate was filtered and washed with water. The dimesitylfurazan oxide (**4**) thus obtained (2.4 g, 75%, mp 130°) was almost pure. One recrystallization from ethanol yielded a product, mp 132°, which did not depress the melting point of a specimen prepared from mesitonitrile oxide. The infrared spectra of both samples were strictly superimposable.

Registry No.—**3**, 16031-57-5; **4**, 16031-58-6; **7**, 16031-59-7; **8**, 16031-60-0; **9**, 16031-61-1; **10**, 4746-81-0; **11**, 16031-62-2; N,N′-diacetylmesityldiimine 16031-64-4; N,N′-dibenzoylmesityldiimine, 16031-63-3.

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A Study of the Interaction of 1,3-Diaxial Sulfur Atoms

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A series of ethylene thioketals was prepared by the reaction of 1,3-cyclohexanediones and phloroglucinol with ethanedithiol. The uv spectra and physical properties of these compounds are discussed.

In the reaction between 5,5-dimethyl-1,3-cyclohexanedione and ethanedithiol the bisthioketal, 13,13-dimethyl-1,4,8,11-tetrathiadispiro[4.1.4.3]tetradecane, was isolated. It was noted that compound **4** possessed ultraviolet absorption at 246 mμ which was similar to values reported for acyclic mercaptols. The absorption for cyclic thioketals can be ascribed to resonance interactions as proposed by Fehnel and Carmack.[2]

The distance between the 1,3-diaxial sulfur atoms in **4** is relatively close to that between sulfur atoms in the thioketal ring. This suggested the possibility of the occurrence of 1,3-diaxial sulfur interactions as well as the interactions present within the thioketal ring.

A series of mono-, di-, and triethylene thioketals was synthesized and the ultraviolet spectra studied to determine if 1,3-diaxial and 1,3,5-triaxial sulfur orbital interactions do exist. The observed maxima and extinction coefficients are given in Table I.

The results indicate that there is no marked interaction between 1,3-diaxial sulfur atoms since the long wavelength absorption at 246 mμ remains constant for the series of thioketals studied. The additive effect in the molar extinction coefficients are approximately the values which would be expected with multiple chromophores. However, a proportionately larger increase in the molar extinction coefficient was observed on the introduction of a second thioketal grouping β to the first in the parent compound 1,4-dithiaspiro[4.5]decane (**1**). A simple additive effect would give an extinction coefficient of ~630 but the observed values were 748, 729, and 728, respectively, for **2**,

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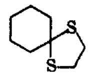
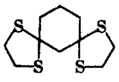
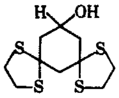
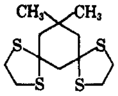
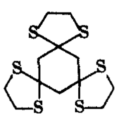
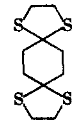
(1) Taken in part from the dissertation presented by J. L. Diebold, 1964, to the Graduate School of the University of Kansas in partial fulfillment of the requirements for the Ph.D. Degree.

(2) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **71**, 84 (1959).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA[a]

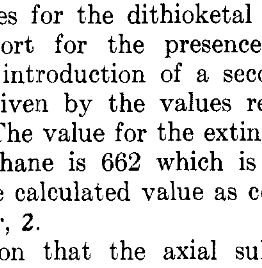
Compd		1,2-Dichloroethane[b]		Acetonitrile[c]	
		λ, mμ	ε[d]	λ, mμ	ε[d]
1[e,f]		246	315	242	295
2		246	758	243	628
3		246	729	243	622
4		246	723	244	621
5		246	1030		
6[f]		246	662	243	560

[a] Recorded on a Bausch and Lomb Spectronic 505. [b] Reagent grade. [c] Spectrograde. [d] Molar extinction coefficient. [e] We are indebted to M. P. Mertes for a sample. [f] λ_{max}^{MeOH} 243 mμ (ε 283).

3, and 4, thus indicating a deviation of approximately 15% from the theoretical value.

When a third thioketal, compound 5, was introduced β to the other two, it appears that the chromophoric increment is about the predicted value obtained by adding the values for the dithioketal and the monothioketal. Support for the presence of a definite effect upon the introduction of a second thioketal β to the first is given by the values recorded for the 1,4 isomer, 6. The value for the extinction coefficient in 1,2-dichloroethane is 662 which is a deviation of only 32 from the calculated value as compared to 128 in the 1,3 isomer, 2.

The assumption that the axial sulfur atoms can interact requires the cyclohexane ring to remain in a true chair or certain boat conformations. The very close approach of the 1,3-diaxial sulfur atoms and their large bulk could cause distortion of the cyclohexane ring. This possibility is increased by the introduction of methyl 1,3-nonbonded interactions as would occur in 4. The appearance of only one signal for the *gem*-dimethyl group in the nmr spectrum of 4 could indicate such distortion results in the equalization of the environments of the methyl groups. The most likely conformation would then be a twist or skew-boat in which the sulfur atoms are at a maximum distance from each other. The nmr signal is not sufficient proof of the presence of a twist form, since the possibility exists that the thioketal sulfur atoms could modify the magnetic susceptibility of one of the methyl groups enough to cause both methyl peaks to be superimposable or the signal could be due to rapid ring inversion.



4

The 1,3,5-trisubstituted system (5) would be expected to have the possibility of resonance stabilization in the 1,3,5-triaxial form owing to an overlap of the sulfur orbitals. However, the steric crowding of the sulfur atoms may cause ring distortion which would prevent orbital overlap. It is apparent that no major interaction of sulfurs other than that within the thioketal occurs in this system.

It was possible to oxidize 4 to the corresponding tetrasulfone in the presence of trifluoroperoxy acetic acid. A similar attempt to oxidize 5 to the corresponding hexasulfone failed to go to completion, but produced a mixture having nine to eleven oxygens present per molecule.

Experimental Section[3]

1,4,8,11-Tetrathiadispiro[4.1.4.3]tetradecane (2).—Boron trifluoride etherate (6.33 g, 0.0446 mol) was added during 1.5 hr to a stirred solution of 2.5 g (0.0223 mol) of dihydroresorcinol and 4.2 g (0.0446 mol) of ethanedithiol in 60 ml of tetrahydrofuran at room temperature. After 2 days the solution was diluted with 250 ml of hot water and the white crystalline precipitate was collected. Recrystallization from isopropyl ether gave 1,4,8,11-tetrathiadispiro[4.1.4.3]tetradecane in a 80% yield: mp 158–158.5°; for uv data see Table I; nmr, δ 3.28 (H_a see structure 4), 2.73 H_b, 1.93 H_c.

Anal. Calcd for $C_{10}H_{16}S_4$: C, 45.41; H, 6.10; S, 48.49. Found: C, 45.45; H, 6.12; S, 48.28.

1,4,8,11-Tetrathiadispiro[4.1.4.3]tetradecan-13-ol (3).—Boron trifluoride etherate (3.78 g, 0.0265 mol) was added during 15 min to a stirred solution of 1.70 g (0.0133 mol) of dihydrophloroglucinol and 2.5 g (0.0265 mol) of ethanedithiol in 20 ml of glacial acetic acid at room temperature. After 1 day the product was collected. The residue from the evaporated mother liquor and the product were both washed with hot water to remove any starting material. Recrystallization from 1,2-dichloroethane gave 2 g of white crystalline 1,4,8,11-tetrathiodispiro[4.1.4.3]-tetradecan-13-ol in a 54% yield: mp 208–209°; for uv data see Table I; nmr, δ 3.31 H_a, 2.66 H_b.

Anal. Calcd for $C_{10}H_{16}S_4O$: C, 42.82; H, 5.75; S, 45.73. Found: C, 43.04; H, 5.89; S, 45.70.

13,13-Dimethyl-1,4,8,11-tetrathiadispiro[4.1.4.3]tetradecane (4).—Boron trifluoride etherate (5.63 g, 0.0396 mol) was added during 30 min to a stirred solution of 4.15 g (0.0441 mol) of ethanedithiol and 5 g (0.0357 mol) of 5,5-dimethyl-1,3-cyclohexanedione in 75 ml of glacial acetic acid and heated to 70°. After 1 day the product was collected. Concentration of the filtrate gave a total yield of 3 g (29%) of 13,13-dimethyl-1,4,8,11-tetrathiadispiro[4.1.4.3]tetradecane. Recrystallization from glacial acetic acid gave white needles: mp 176.5–177°; for uv data see Table I; nmr, δ 3.28 H_a, 2.68 H_b, 1.98 H_c, 1.15 H_d.

Anal. Calcd for $C_{12}H_{20}S_4$: C, 49.27; H, 6.89; S, 43.84. Found: C, 49.33; H, 6.75; S, 43.66.

1,4,8,11,14,17-Hexthiatrispiro[4.1.4.1.4.1]octadecane (5).—Phloroglucinol (5.0 g, 0.0308 mol) and 8.69 g (0.0924 mol) of ethanedithiol were dissolved in 75 ml of glacial acetic acid to which was added 17.46 g (0.123 mol) of boron trifluoride etherate during 15 min. The solution was magnetically stirred at room temperature for 24 hr and the product collected. Five successive filtrations gave more product from the filtrate upon standing. The combined yield was 0.87 g (8%). Recrystallization from 1,2-dichloroethane gave white crystals: mp 287–287.5°; for uv data see Table I; nmr, δ 3.28 H_a, 2.70 H_b.

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(3) Melting points were obtained on a calibrated Thomas–Hoover Unimelt and are corrected. Nmr data were recorded on a Varian Associates Model A-60 spectrometer using tetramethylsilane as an internal standard and using tetramethylsilane as an internal standard and using $CDCl_3$ as the solvent. Microanalyses were performed by Drs. G. Weiler and F. B. Strauss, Oxford, England, and Huffman Microanalytical Laboratories, Wheatridge, Colo.

Anal. Calcd for $C_{12}H_{18}S_6$: C, 40.64; H, 5.12; S, 54.25. Found: C, 40.76; H, 5.04; S, 54.06.

13,13-Dimethyl-1,4,8,11-tetrathiadispiro[4.1.4.3]tetradecane 1,1,4,4,8,8,11,11-Octaoxide.—Trifluoroperoxyacetic acid was prepared by adding trifluoroacetic anhydride (84 ml, 0.398 mol) during 15 min to a stirred, ice-cold solution of 15 ml of chloroform and 14 ml (0.50 mol) of 90% hydrogen peroxide. After 20 min this solution was added during 30 min to a stirred, ice-cold suspension of 2.0 g (0.00684 mol) of 13,13-dimethyl-1,4,8,11-tetrathiadispiro[4.1.4.3]tetradecane, 7 g (0.049 mol) of disodium hydrogen phosphate and 20 ml of chloroform. The slurry was refluxed for 12 hr and poured into 500 ml of ice–water and 100 ml of chloroform. The heterogeneous solution was made neutral with sodium bicarbonate and shaken. Filtration and washing with chloroform and water gave 1.91 g of white microcrystalline 13,13-dimethyl-1,4,8,11-tetrathiadispiro[4.1.4.3]tetradecane 1,4,4,8,8,11,11-octaoxide (66%), mp 260–280° with sintering. The addition of methanol caused two crystalline modifications having different solvent properties to separate: methanol soluble, mp 230–245° with sintering; methanol insoluble, mp 260–280° with sintering. Their infrared spectra (KBr) were different in the 700–950-cm^{-1} region, but identical at 1125 and 1335 cm^{-1}, indicative of a sulfone.

Anal. Calcd for $C_{12}H_{20}S_4O_8$: C, 34.27; H, 4.79; S, 30.50. Found: C, 34.86; H, 5.09; S, 30.42.

Registry No.—**1**, 177-16-2; **2**, 7490-36-0; **3**, 15856-34-5; **4**, 15732-74-8; **5**, 15814-64-9; **6**, 311-37-5; 13,13-dimethyl-1,4,8,11-tetrathiodiaspiro[4.1.4.3]tetradecene 1,1,4,4,8,8,11,11-octaoxide, 15814-66-1.

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Evaluation of Steric Effects in Additions to Substituted Cyclohexenes[1]

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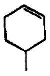
A number of mono- and dialkylsubstituted cyclohexenes have been prepared and subjected to hydroboration under carefully controlled conditions. The alcohol product distributions, obtained on basic peroxide oxidation of the intermediate alkylborane mixtures, are used to assess the source of the steric effects involved in the addition of borane to the cyclohexenyl systems. It is found that in the 1-substituted 4-*t*-butylcyclohexenes, except the 1,4-di-*t*-butyl compound, there is a preference for addition *cis* to the 4-*t*-butyl group. This is attributed to a more prominent steric effect imposed by the axial 4-hydrogen, the effect of which is greater at the 2 position than at the 1 position, and the axial 5-hydrogen, the effect of which is greater at the 1 position than the 2 position. These steric effects are enhanced on substitution of methyl for hydrogen at these positions or by the use of bulky hydroborating agents. Alkyl groups in the 3 position give rise to direct steric effects, effects due to distortion about C_3, and inductive effects. The anomalous results obtained in the hydroboration of 1,4-di-*t*-butylcyclohexene are attributed to steric effects imposed by specific rotational conformations about the C_1-*t*-butyl carbon bond, an effect which is also present in 1-isopropylcyclohexenyl systems. The results are discussed in terms of the proposed distortion of the 4-*t*-butylcyclohexene system by Rickborn and Lwo, and the applicability of the Garbisch model for additions to substituted cyclohexenes in which torsional angle effects in going to the transition state are considered to be important.

Numerous studies of the addition of a variety of reagents to simple substituted cyclohexenes have been reported in the literature. However, very few exhaustive kinetic and stereochemical studies involving these reactions have been carried out. Kwart and Miller[4] have measured the second-order rate constants for the addition of 2,4-dinitrobenzenesulfenyl chloride to a number of 4-mono- and 4,5-disubstituted cyclohexenes. These authors stated "the effect of the substituents of the 4-monosubstituted cyclohexenes on the rate of addition of 2,4-dinitrobenzenesulfenyl chloride is predominantly electronic in nature."[4] A portion of the data of Kwart and Miller is included in Table I for comparison with the relative rates of other addition reactions.

Rickborn and Lwo[5] have measured the rates and determined the stereochemistry of epoxidation of remotely substituted alkyl cyclohexenes (see Table I). These authors suggest "that the effects of remote alkyl groups are primarily steric rather than inductive in nature." The results for 4-methylcyclohexene were rationalized on the basis of a rate retarding steric effect contributed by the conformation with the *axial* methyl group. In order to explain the results of epoxidation of 4-*t*-butylcyclohexene, Rickborn and Lwo[5] invoked an unspecified distortion of the cyclohexene system by the bulky *t*-butyl group.

TABLE I
RELATIVE RATES OF ADDITIONS TO 4-SUBSTITUTED CYCLOHEXENES

	2,4-Dinitrobenzene-sulfenyl chloride 30° [a]	Epoxidation at 25° [b]	Diimide reduction at 80° [c]
	100	100	100
	81.2	81 (53.6% *trans* product)	90[d]
	89.7	94 (39.5% *trans* product)	95

[a] See ref 4. [b] See ref 5. [c] E. W. Garbisch, S. M. Schildkraut, and D. M. Patterson, *J. Amer. Chem. Soc.*, **87**, 2932 (1965). [d] Data derived from the 1-*t*-butylcyclohexene and 1-*t*-butyl-4-methylcyclohexene.

Consistent with the observation of Rickborn and Lwo on the stereochemistry of epoxidation of 4-*t*-

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[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (PRF 1225-A1, 3). (b) Taken from the Ph.D. Thesis of F. M. K., University of Notre Dame, 1966. (c) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] Alfred P. Sloan Research Fellow, 1967–1969.

[3] National Science Foundation Predoctoral Fellow, 1963–1965; Lubrizol Fellow, 1965–1966.

[4] H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961).

[5] B. Rickborn and S. Y. Lwo, *J. Org. Chem.*, **30**, 2212 (1965).