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Registry No.—**3**, 2564-83-2; **4d**, 51805-90-4; **7**, 51805-91-5; **8**, 51805-92-6; **9**, 51805-93-7; **10**, 51805-94-8; **15**, 50348-93-1; **16**, 51805-95-9; **17**, 34372-02-6; **19**, 51805-96-0; **20**, 51805-97-1; **21**, 51805-98-2; **22**, 51805-99-3; **23**, 51806-00-9.

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Concentration Effects in the Photochemical Syn–Anti Isomerization of an Oxime Ether

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Upon irradiation with ultraviolet light, the *O*-methyl oxime ethers of 2-acetonaphthone undergo facile syn–anti photoisomerization. At low concentrations the syn isomer predominates in the photostationary state. High oxime ether concentrations, however, were found to enhance the fraction of the anti isomer in the photoequilibrium. Evidence supporting the involvement of the singlet state was obtained from fluorescence quenching studies and photosensitized isomerization experiments. Fluorescence quenching of both isomers by 1,3-cyclohexadiene was found to be more sensitive toward the quencher concentration than chemical quenching. The excited syn isomer was much less sensitive toward chemical quenching and showed a less intense emission than the corresponding anti form. The data obtained are consistent with the involvement of an excimer which is capable of inducing efficient syn–anti isomerization and whose decay ratio differs from that of excited monomer.

The thermal[3-9] and photo-[10-33] interconversions of the syn and anti isomers of imines are a subject of long-standing interest. The mechanism for the thermal interconversion of imine diastereomers is currently the subject of considerable debate,[34-45] and has been considered in terms of either a planar inversion mechanism or a rotation mechanism. The rotation or torsion mechanism involves a twisting about the C═N double bond. The inversion mechanism, on the other hand, is characterized by an increase in the angle of the C═N-C bond from approximately 120° in the ground state to 180° in the transition state. Evidence obtained from studies of substituent effects (steric and electronic) suggests that most simple imines interconvert by the inversion mechanism,[44] although some of the results obtained have been considered to be inconclusive.[34-36]

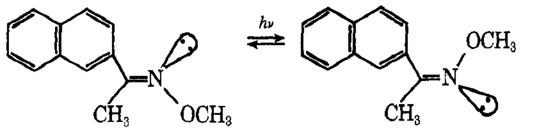
The mechanism by which the syn and anti isomers of imines are interconverted in the excited state is even more complicated. Whether isomerization about the C═N double bond proceeds by rotation or linear inversion remains to be clarified. A major complication with the photochemical studies is that the thermal barrier between the two diastereomers of most imines is sufficiently low that the photochemically induced shift in the configurational equilibrium is only temporary at ambient temperatures and is frequently followed by a rapid, thermal relaxation which reestablishes the initial configurational equilibrium between the syn and anti isomers.

In previous work[31] we showed that irradiation of an oxime ether brings about a rapid syn–anti isomerization. The oxime ether molecule is an attractive system for mechanistic photostudies, since the presence of the methoxyl group drastically reduces the rate of thermal interconversion of the syn and anti forms (*i.e.*, $k < 10^{-13}$ at 60°)[3] and allows mechanistic studies to be carried out at ambient temperatures.

In order to secure additional information on the reactivity of the excited state(s) involved in the syn–anti photoisomerization reaction, we decided to study the photochemistry of a naphthyl-substituted oxime ether. It is reasonable to assume that in the naphthyl oxime ether system, the excitation energy will be heavily localized on the naphthyl portion of the molecule. Concentration of the excitation at one end of the molecule seemed a possible way of modifying the photoisomerization reaction. In the present paper we report on some aspects of the direct and sensitized isomerization of the syn and anti isomers of 2-acetonaphthone oxime *O*-methyl ether, where we note that marked discrepancies exist between predicted and measured photostationary states. The results obtained are of fundamental interest by virtue of their superficial parallels to and mechanistic differences from the corresponding situation in olefin photochemistry.[46,47]

Results and Discussion

The anti *O*-methyl ether of 2-acetonaphthone oxime (**2**) was synthesized by treating 2-acetonaphthone with methoxylamine hydrochloride according to the procedure of Karabatsos and Hsi[48] [nmr ($CDCl_3$) δ 2.36 (s, 3 H), 4.12 (s, 3 H)]. The corresponding syn isomer **1** was prepared by irradiation of **2** in pentane using 3130-Å light [nmr ($CDCl_3$) δ 2.28 (s, 3 H), 3.94 (s, 3 H)]. The two isomers could readily be separated by vapor phase chromatography and their thermal stability was established by heating each isomer separately at 140° and noting the absence of isomerization. Thermal equilibration of the two compounds could be achieved by iodine catalysis. In both cases, the equilibrium is, within experimental error, predominantly on the anti-isomer side (96% anti and 4% syn oxime ether). The ultraviolet absorption spectra of both the syn and anti forms resembled that of naphthalene.



2 **1**

Irradiation of degassed pentane (or benzene) solutions of syn (or anti) oxime ethers (**1** or **2**) at 3130 Å led to photostationary states whose composition varied, as shown in Table I, from 64% syn at [oxime ether] = 0.003 *M* to 42% syn at [oxime ether] = 1.35 *M*. The analyses by vpc were reproducible typically to better than ±0.3% in the comparison of the mean value of replicate samples and to ±0.5% for the average deviation from the mean of replicate injections of the same sample; the modest changes we observe are thus unquestionably real. The data obtained (Table I) indicate that the final photostationary state composition is dependent on both the temperature maintained and the concentration and solvent used during the course of the irradiation [*i.e.*, [syn]/[anti] at 0.1 *M* pentane = 0.92 ± 0.03 at 25° and 1.20 ± 0.05 at 80°; [syn]/[anti] = 1.80 ± 0.06 at 0.003 *M* (25°), 1.11 ± 0.05 at 0.05 *M* (25°), and 0.72 ± 0.04 at 1.35 *M* (benzene, 25°)]. These results show that high oxime ether concentrations enhance the fraction of the anti isomer in the photostationary state. High temperatures, however, tend to diminish the fraction of the thermodynamically more stable anti form. This type of behavior was not observed in the photoisomerization of the related acetophenone oxime ether system.[31]

The concentration dependence in the oxime ether system was also reflected in the quantum yields for photoisomerization. Quantum yields for the isomerization reaction were determined using benzophenone–benzhydrol actinometry.[49] The results obtained (Table I) indicate that as the total concentration of the oxime ether increased, the quantum efficiency of the anti → syn isomerization ($\Phi_{A \rightarrow S}$) decreased while the $\Phi_{S \rightarrow A}$ increased. The ratio of the quantum efficiencies ($\Phi_{A \rightarrow S}/\Phi_{S \rightarrow A}$) was found to vary in a manner analogous to the variation of the photostationary state ratio. The sum of the quantum yields, however, remained constant.

Table I
Quantum Yield and Photostationary State Dependence of Oxime Ethers 1 and 2 on Concentration, Solvent, and Temperature[a–c]

Total concn, *M*	Syn/Anti Pentane	Syn/Anti Benzene	$\Phi_{A \rightarrow S}{}^d$	$\Phi_{S \rightarrow A}{}^d$	Φ_A/Φ_S
0.003	1.80				
	1.86 (80°)				
0.008	1.67				
0.012	1.59	1.64			
0.023	1.34	1.57	0.56	0.35	1.60
0.042	1.18	1.45	0.48	0.36	1.41
0.05	1.11		0.53^e	0.49^e	1.08^e
	1.32 (80°)				
0.08		1.31	0.46	0.39	1.18
0.10	0.92				
	1.20 (80)				
0.17		1.14	0.42	0.37	1.14
0.34		0.96	0.42	0.41	1.02
0.67		0.79	0.40	0.46	0.87
1.35		0.72	0.39	0.48	0.81

[a] 3130-Å light. [b] The analyses by vpc were reproducible typically to better than ±0.5% in the comparison of the mean value of replicate samples. [c] All values reported at 25° unless otherwise stated. [d] All quantum yields determined in benzene unless otherwise stated. [e] Determined in pentane solution.

Two possibilities come to mind in seeking an explanation for the cause of the syn/anti isomer variation. These are (1) association between ground-state molecules which give rise to dimers and higher aggregates, and (2) specific interactions between ground-state and excited oxime ether molecules. With respect to the first possibility, theoretical considerations indicate that association should lead to a new absorption at longer or shorter wavelengths than that due to monomer.[50,51] We have examined both the syn and anti isomers over a wide concentration range and have found no evidence of spectral change in the ultraviolet region; both the position of the absorption bands and the extinction coefficients are, within experimental error, independent of the concentration. Since no evidence for ground-state complexation could be found by uv as well as ir and nmr spectroscopy, it would seem as though the observed variation in the photostationary state is due to interactions between excited and ground-state molecules.[52]

The interaction between excited and ground-state molecules is a well-documented phenomenon.[53-56] These interactions will be expected to be somewhat dependent on the temperature and solvent system employed.[53] The data obtained above are consistent with the involvement of an excimer which is capable of inducing efficient syn–anti isomerization and whose "decay ratio" differs from that of the excited monomer. The variation of the photostationary state composition as a function of temperature can be attributed to the dissociation of the excimer with re-formation of the excited monomer at higher temperatures. The equilibrium associated with excimer formation and its corresponding "decay ratio" will also be exected to be influenced by the nature of the solvent system used. Excimers have been reported to play an important role in the photoisomerization of certain olefinic systems.[57-60] In these cases it was found that a high olefin concentration also enhances the fraction of the trans isomer in the photostationary state.

In this connection, it is worthy to note that the fluorescence emission spectrum of oxime ether **1** is subject to concentration quenching. The fluorescence emission curve for **1** at 0.03 *M* was essentially identical in shape and

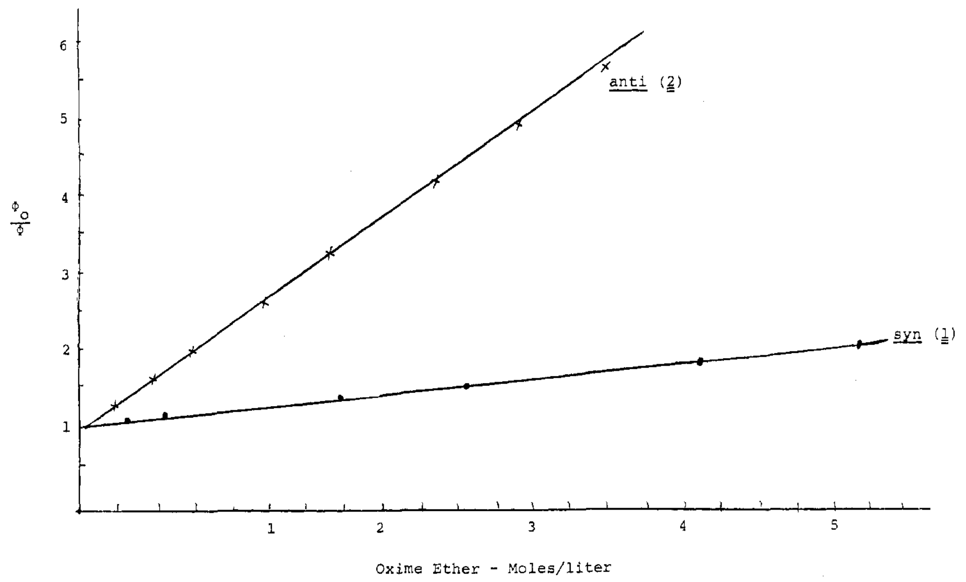


Figure 1. 1,3-Cyclohexadiene quenching of the fluorescence of the syn and anti isomers of the *O*-methyl ether of 2-acetonaphthone oxime in pentane (25°).

wavelength with that of naphthalene. Most importantly, a new component (*ca.* τ 500 nm) became evident in the fluorescene spectrum as the concentration of the syn isomer increased (0.1–1.2 *M*). This new fluorescence component is similar to that observed with other systems which involve associative interactions and most likely derives from excimer formation.[61]

In order to determine whether the phosphorescence emission spectrum of **1** (and/or **2**) showed a similar concentration dependence, we examined the emission spectra of the oxime ethers at 77°K in an EPA glass. Surprisingly, both isomers showed no phosphorescence. The lack of phosphorescence would imply that either the intersystem crossing efficiency of the oxime ethers is extremely low or else the triplet state of the oxime ethers undergoes nonradiative decay at a faster rate than radiative emission. To test these possibilities, an attempt was made to sensitize the phosphorescence emission of the oxime ethers. This was done by irradiating a 1:1 mixture of benzophenone and the oxime ether at 77°K in an EPA glass. The sample tube was irradiated under conditions where 100% of the light was absorbed by benzophenone (*i.e.*, 3660 Å). The results obtained showed that benzophenone's emission was completely quenched and no new emission from the oxime ethers appeared. This experiment indicates that nonradiative decay from the triplet state (*i.e.*, syn $\rightleftarrows$ anti photoisomerization) proceeds at a faster rate than radiative decay. Consequently, the lack of phosphorescence from the oxime ethers does not necessarily reject the involvement of a triplet state in the direct irradiation (*vide infra*).

A major point which needed to be established is whether the concentration effects noted in the photoisomerization and fluorescence experiments are derived from a common intermediate. In order to establish this point, quenching experiments using 1,3-cyclohexadiene as a singlet quencher[62] (1.0–3.0 *M*) were carried out. Addition of 1,3-cyclohexadiene to pentane solutions of the oxime ethers resulted in substantial quenching of the fluorescence emission of both **1** and **2**. The data are plotted in the usual Stern–Volmer fashion and are shown in Figure 1. 1,3-Cyclohexadiene was also found to quench the syn-anti photoisomerization. Figure 2 shows the Stern–Volmer plot for 1,3-cyclohexadiene quenching of the syn-anti isomerization. Slopes were calculated by least-squares analysis of the data. The quenching slopes obtained with 1,3-cyclohexadiene are $k_q\tau(\mathbf{1})_{\text{isom}}$ = 0.04, fluorescence quenching = 0.13 and $k_q\tau(\mathbf{2})_{\text{isom}}$ = 0.30, fluorescence quenching = 1.20 for the syn (**1**) and anti (**2**) oxime ethers, respectively. The results demonstrate that the anti isomer is more sensitive to fluorescence quenching (*i.e.*, factor of 9.2) than the corresponding syn form. The difference in quenching efficiency between the anti and syn forms was slightly smaller (*i.e.*, 7.5) when the photoisomerization reaction was monitored. It is interesting to note that chemical quenching is only one-quarter as efficient as fluorescence quenching. This phenomenon is not totally unprecedented, as variations in fluorescence *vs.* chemical quenching have been observed by others.[63]

One interpretation of the above observations is that the photoisomerization reaction does not proceed from a singlet state but rather involves a short-lived reactive triplet which is quenched at high quencher concentration. If this were true, then the lack of correspondence between the chemical and fluorescence quenching would be expected, since two different excited precursors would be involved. That this is not the case was shown by triplet sensitization

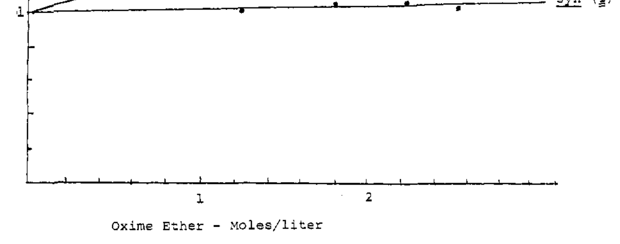


Figure 2. 1,3-Cyclohexadiene quenching of the syn (**1**)–anti (**2**) photoisomerization.

experiments in which benzophenone was used as the sensitizer (*i.e.*, 3660-Å source). The quantum yield for the benzophenone-sensitized anti → syn isomerization ($\Phi_{A\rightarrow S}$) at 0.05 *M* was 0.37 + 0.02 in the 4–5% reaction range, while that for syn → anti ($\Phi_{S\rightarrow A}$) was 0.51. The ratio of triplet quantum yields ($\Phi_{A\rightarrow S}/\Phi_{S\rightarrow A}$) is 0.73, in good agreement with the experimental value of the sensitized photostationary state (0.77). If decay from a common state is involved in both the sensitized and unsensitized experiments, the decay ratio should be the same for the two processes. It should be pointed out that the triplet-sensitized isomerization, in contrast to the unsensitized isomerization, was independent of the initial oxime ether concentration. The difference between the two numbers [*i.e.*, 0.73 (triplet) and 1.08 (singlet)] is an indication that crossing to triplets is not the sole fate of excited oxime ether singlets. The closeness of the above values could be construed to mean that the isomerization induced by direct irradiation is also passing in part through the triplet state. It should be emphasized, however, that the closeness of the values does not demand that the triplet state of the oxime ether be involved in the direct isomerization. As was pointed out by Saltiel,[64] the correlation of the natural decay ratios in sensitized and unsensitized photoisomerization processes may be fortuitous.

An alternate rationale to account for the variation in fluorescence *vs.* chemical quenching observed with 1 would involve the partial involvement of a short-lived unquenchable precursor to photoisomerization. This may possibly be an upper excited state or a nonquenchable upper vibrational level of the first excited state (singlet or triplet). The diminished 1,3-cyclohexadiene quenching of the isomerization reaction would then reflect a combination of partial quenching of isomerization from the vibrationally equilibrated S_1 state and zero quenching of reaction from the upper vibrational levels of S_1 or an upper excited state. In order to test for the possible involvement of upper excited states in the photoisomerization reaction, we examined the quantum efficiency of the oxime ether isomerization using 2537-Å light. Surprisingly, the quantum yields for isomerization at 2537 Å showed a substantial diminution in value (*i.e.*, $\Phi_{A\rightarrow S} = 0.28$, $\Phi_{S\rightarrow A} = 0.27$) when compared to the values obtained at 3130 Å (*i.e.*, $\Phi_{A\rightarrow S} = 0.53$, $\Phi_{S\rightarrow A} = 0.49$). This might at first glance seem to be inconsistent with the participation of upper vibrational or excited states. However, by using short-wavelength light the possibility exists that both the n-π* (or π-π*) state of the oxime ether and the π-π* state of the naphthalene moiety are populated. The lower quantum efficiency may be attributed to either an incomplete internal energy transfer, a diminished intersystem crossing from the naphthyl π-π* state(s) to the imine excited state(s), or a radiationless decay path of the excited naphthyl state(s) which maintains the geometric integrity of the oxime ether. Another possibility which can account for the difference between fluorescence and chemical quenching is to assume the involvement of an exciplex in the quenching reaction. All that would be necessary to explain the preferred fluorescence quenching is to assume that exciplex decay will result in the partial isomerization of the oxime ether. The overall effect would then be less efficient chemical quenching than fluorescence quenching.

Considerable information has now been accumulated for the photochemical syn–anti isomerization of the oxime ether of 2-acetonaphthone. The more readily derived facts about the photoisomerization reaction are the following. (a) At low concentration the syn isomer predominates in the photostationary state. (b) High oxime ether concentrations tend to enhance the fraction of the anti isomer in the photostationary state. (c) Evidence supporting the involvement of the singlet state was obtained from fluorescence quenching studies and photosensitized isomerization experiments. The data also indicate that the fluorescence quenching of both isomers by 1,3-cyclohexadiene is more sensitive than chemical quenching. (d) The fluorescence and photoisomerization quenching studies also show that the excited syn isomer is less sensitive to collisional interaction than the corresponding anti form. The intensity of emission from the syn isomer was found to be much less (*i.e.*, *ca.* factor of 10) than that from the anti isomer. These observations imply that the excited spectroscopic state of the syn isomer has a much shorter lifetime than the related anti form.

The mechanism we propose here to explain these observations (see below) involves excitation of the oxime ether (X_o = syn or anti oxime ether) to its spectroscopic singlet state followed by formation of a twisted excited state (P*).

$$
\begin{gathered}
X_o \xrightarrow{h\nu} X^{*1} \\
X^{*1} \xrightarrow{k_f} X_o + h\nu^1 \\
X^{*1} \xrightarrow{k_d} X_o \\
X^{*1} \xrightarrow{k_1} P^* \\
x^{*1} + X_o \xrightarrow{k_2} [X\text{–}X]^{*1} \\
[X\text{–}X]^{*1} \xrightarrow{k_3} \alpha S_o + \beta A_o \\
P^* \xrightarrow{k_4} S_o \\
P^* \xrightarrow{k_5} A_o \\
P^* + X_o \xrightarrow{k_6} \alpha' S_o + \beta' A_o \\
X^{*1} + C_o \xrightarrow{k_7} [X\text{–}C_o]^{*1} \\
[X\text{–}C_o]^{*1} \xrightarrow{k_8} C_o + \alpha'' S_o + \beta'' A_o
\end{gathered}
$$

The spectroscopic singlet state can decay (k_d), fluoresce (k_f), or undergo collisional interaction with a ground-state molecule (k_2) to produce an excimer. The excimer's decay ratio differs from that of monomer (P* or possibly X^{*1}) and leads to preferential formation of the thermodynamically more stable anti isomer (A_o). In this scheme α and β represent partitioning factors. This rationale is reinforced by quantum yield studies which show that the $\Phi_{A\rightarrow S}$ decreases while the $\Phi_{A\rightarrow S}$ increases with increasing substrate concentration. The formation of the syn isomer (S_o) would also be expected to result from collisional quenching; however, the partitioning coefficient seems to favor the anti form. Quenching of the spectroscopic singlet by 1,3-cyclohexadiene (C_o) may involve an exciplex. Other reactions involving collisional quenching of the twisted state (P*) by a ground-state molecule (*i.e.*, k_6) may well occur, but the experimental data are not accurate enough to determine this. It should be noted here that, while the mechanism outlined above adequately accounts for the observations, it may be incomplete. For example, the isomerization may also proceed by inversion from the spectroscopic singlet state or pass, in part, through a reactive triplet or an upper excited state.

Experimental Section

Syn and Anti *O*-Methyl Ethers of 2-Acetonaphthone Oxime. A mixture containing 40.5 g of 2-acetonaphthone and 22.1 g of methoxylamine hydrochloride in 500 ml of 95% ethanol which contained 360 g of sodium acetate trihydrate was heated at reflux for 12 hr. Removal of the solvent under reduced pressure left 45 g (97%) of a solid which was recrystallized from ethanol to give the anti *O*-methyl ether of 2-acetonaphthone oxime (2) as a white, crystalline solid, mp 89.5–90°.

Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.71; H, 6.63; N, 7.00.

The infrared spectrum of this material (KBr) showed a series of strong bands at 3.40, 6.22, 8.84, 9.30, 9.55, 11.00, 11.18, 11.60, 12.00, and 13.45 μ. The nmr spectrum ($CDCl_3$) showed sharp singlets at δ 2.36 (3 H) and 4.12 (3 H), and contained a multiplet centered at δ 7.7 (7 H). The ultraviolet spectrum (pentane) exhibited maxima at 338, 295, 283, 274, 249, and 238 nm (ϵ 140, 15,100, 17,400, 14,000, 36,770, and 40,180). The mass spectrum showed the molecular ion at m/e 199 and contained major peaks at m/e 184, 169, 158, 128, 127 (base), and 77.

The corresponding syn oxime ether (1) was prepared by irradiating the anti isomer in pentane at 3100 Å. The mixture of isomers was separated by column chromatography. The syn isomer was further purified by distillation at 90–100° (0.01 mm). The syn isomer was a low-melting solid, mp 25–26°. Analysis of the low-melting solid by glpc using a 0.25 in. × 10 ft copper column packed ing solid by glpc using a 0.25 in. × 10 ft copper column packed with 10% FS-1265 on Diasaport S at 215° revealed that the solid was better than 99% isomerically pure. The infrared spectrum (neat) of 1 showed a series of strong bands at 3.30, 3.42, 3.60, 6.19, 6.25, 6.65, 6.81, 6.95, 7.29, 9.12, 9.50, 11.10, 12.20, and 13.40 μ. The nmr spectrum ($CDCl_3$) showed sharp singlets at δ 2.28 (3 H) and 3.94 (3 H) and also contained a multiplet centered at δ 7.70 (7 H). The ultraviolet spectrum (pentane) exhibited maxima at 224 (ϵ 36,000), 279 (ϵ 8400), and 337 nm (ϵ 110). The mass spectrum showed the molecular ion at m/e 199 and contained major peaks at m/e 184, 169, 158, 128, 127 (base), and 77.

Determination of Photostationary State. Solutions containing the substrate at a fixed concentration in a chosen solvent were irradiated through Pyrex culture tubes at 3130 Å. In these studies, a 1-cm path of 0.002 *M* potassium chromate in a 1% aqueous solution of potassium carbonate was used to isolate the 3130-Å region of the medium-pressure (450-W) Hanovia lamp.[65] All samples were degassed using a vacuum line which achieved a pressure of $<5 \times 10^{-4}$ mm. In every case the photostationary states were approached from both sides and duplicate samples were measured to ensure that the actual stationary composition had been reached.

Quantum Yield Determinations. Solutions were prepared in various solvents as described in the Results and Discussion, and 3.0 ml of each was placed in separate Pyrex culture tubes (13 × 100 mm). Each sample was degassed three times to 0.005 mm and sealed *in vacuo*. Similar results were obtained when samples were degassed by bubbling argon through the solution for 30 min. In a given run all tubes were irradiated in parallel for the same length of time in a "merry-go-round" apparatus which assured that each sample absorbed the same intensity of light. Benzophenone–benzhydrol[49] actinometry was used for the quantum yield determinations. Analyses were performed on a Hewlett-Packard Model 5750 gas chromatograph using a 10% FS-1265 Diasaport S column at 215°. The mole ratio:area ratio response of the instrument was calibrated for the oxime ethers and internal standard, so that yields of product could be measured accurately. The conversions in the oxime ether series were run to 5% or less. The mass balances in these runs were generally better than 98%.

Emission Studies. The emission spectra were made on an Aminco-Bowman spectrophotofluorometer equipped with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. All fluorescence emission spectra were recorded using pentane or cyclohexane as the solvent. The solvent was checked for emission each time a spectrum was recorded and no interference due to solvent was found at any time. Emission intensities were reproducible for different samples prepared from the same solution.

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Observations on Photochemically and Thermally Induced Rearrangements and Fragmentations in 2,5-Dihydrothiophene Derivatives

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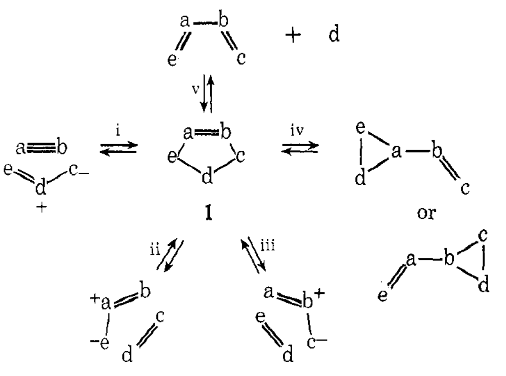
By means of the addition of thiocarbonyl ylides to dimethyl acetylenedicarboxylate, a series of 2,5-dialkylsubstituted 2,5-dihydrothiophenes (**4**) was prepared. These compounds were also oxidized to the respective sulfoxides (**20**) and sulfones (**19**). The compounds **4** undergo ring contraction on irradiation, producing vinyl episulfides. These on desulfurization afford dienes. The sulfoxides **20** provide the same dienes on either irradiation or thermolysis. The only exception is the 2,2,5,5-tetramethyl derivative (**20b**), which gives a complex mixture of products on thermolysis. The sulfones **19** also yield dienes on either irradiation or thermolysis. The stereochemistry of all these reactions has been determined. In complete accord with earlier work, the sulfone thermolyses are completely stereospecific and follow expectations from orbital symmetry considerations. All other reactions studied exhibit lessened stereoselectivity and this is construed as evidence for the intervention of biradical intermediates. In the photochemical reactions of **4** both cisoid and transoid forms of the allylic portion of the biradical formed on cleavage of a carbon-sulfur bond are involved. Related mechanisms are thought to be involved in the photochemical reactions of **19** and **20**. Arguments are advanced that the thermolysis of **19** and **20** involve different mechanisms because the reaction coordinate for the latter reaction cannot be symmetrical; this forces the reaction into a nonconcerted pathway.

Imagine a generalized five-membered heterocycle **1** derivable in principle through a 1,3-dipolar cycloaddition.[1] Routes i–iii (eq 1) all have adequate precedent. Nearly



(1)

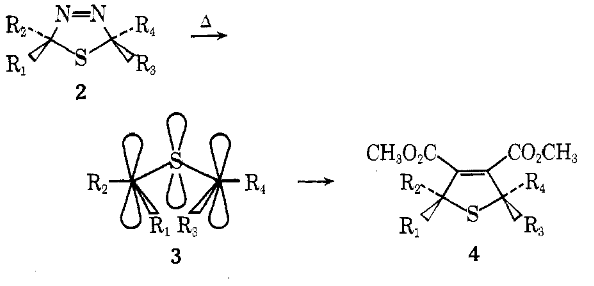
unanimously these reactions involve 1,3-dipole and dipolarophile in their *ground states. Excited states* of **1** could conceivably fragment through one of these pathways. This seems not to be common, however.[2] Although the detailed explanations differ widely from compound to compound, a rationale might be that excited states of **1** must attain a sterically unfavorable antarafacial–suprafacial geometry to fulfill orbital symmetry demands for fragmentations through paths i–iii.[3]

The number of examples is limited, but path iv, a vinyl cyclopropane-like rearrangement,[4] and path v appear to be possible for both ground and excited states. Photochemical examples are restricted chiefly to fragmentations of **1**.[5-7] In these cases orbital symmetry considerations place less stringent steric requirements on the required transition states.

More complete descriptions of the extent to which orbital symmetry factors control these types of reactions, especially those involving excited states, should be forthcoming from stereochemical studies. Such investigations require in practice systems in which carbon atoms with their unique stereochemical properties are present at points at which bonds are made or broken. The common philosophy is that if a given reaction leads to only one of several possible geometrical isomers, all of which are accessible through stereochemically acceptable transition states, and if the isomer formed is that predicted by orbital symmetry factors, this can be considered *ipso facto* as evidence for orbital symmetry control.[3] We offer here the descriptive aspects of the photo- and thermochemistry of 2,5-dihydrothiophenes **4** and their sulfoxide and sulfone derivatives.[8,9] This is a limited study of only one compound type. We hope nevertheless that the results obtained are not only interesting in their own right but lend also some insight into the broader problems hinted at in eq 1.

Results

A. Thermochemistry and Photochemistry of 4. The genesis of compounds **4** lies in the thermally induced ste-



(2)

a, $R_1 = R_4 = t\text{-}C(CH_3)_3$; $R_2 = R_3 = H$
b, $R_1 = R_2 = R_3 = R_4 = CH_3$
c, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
d, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
e, $R_1 = R_4 = C_2H_5$; $R_2 = R_3 = H$
f, $R_1 = R_3 = C_2H_5$; $R_2 = R_4 = H$