

Photochemical Syn–Anti Isomerization about the Carbon–Nitrogen Double Bond

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Abstract: Upon irradiation with ultraviolet light, the *O*-methyl oxime ethers of acetophenone undergo facile syn–anti photoisomerization. The photostationary state ratio obtained by direct irradiation of the syn and anti oxime ethers was 2.20 ± 0.03 . Photoisomerization about the C–N double bond could also be induced by triplet excitation. A photostationary state *vs.* triplet energy of the sensitizer plot shows (1) a high-energy region in which the stationary state ratio is *ca.* 1.5, (2) a gradual increase in the syn/anti ratio from 72 down to 59 kcal of triplet energy, and (3) a sharp decrease from 59 down to 54 kcal. The latter two observations were explained by nonvertical excitation of the acceptor. Analysis of the sensitized quantum yields for the syn–anti isomerization reaction shows that energy transfer to the oxime ethers does not proceed with identical rates. The inefficiency encountered in these sensitized experiments suggests that not all triplet sensitizers are effective in generating a twisted imine triplet. A double sensitization experiment using the oxime ethers and *trans*-stilbene indicates that triplet energy transfer can occur from the oxime ethers to *trans*-stilbene. Since the direct irradiation could not be quenched with high concentrations of piperylene, it would seem as though an electronically excited singlet is the reactive state in the direct isomerization.

One of the most active areas of organic photochemistry has been the study of systems which possess a carbonyl group.^{2–5} As a result of these studies the photochemical transformations of organic molecules containing this functional group have been categorized into a number of primary photochemical processes.⁶ This state of affairs contrasts sharply with the present status of the structurally related imine system, the photochemistry of which is mainly qualitative with relatively little available in the way of quantum yield data and kinetic studies. While photochemical reactions have been observed with a number of systems possessing a C–N double bond,^{7–31} a more

frequently encountered phenomenon for simple imines is a high rate and efficiency of radiationless decay of the excited state.³² The facile deactivation of the imine chromophore can be attributed to rotation about the π bond in the excited state, thereby allowing for dissipation of electronic energy.³³ The photo^{34–56} and

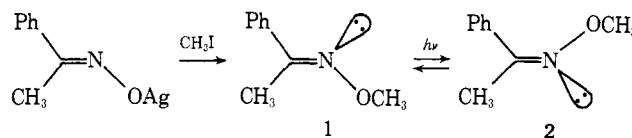
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thermal⁵⁷⁻⁶³ interconversions of the syn and anti isomers of imines are a subject of long-standing interest. Recent investigations into the factors influencing the ease of thermal isomerization about the C-N double bond have shown that the interconversion barrier is remarkably sensitive to the attached substituent groups.^{57,58} For example, among imino compounds derived from benzophenone, changes in groups attached to nitrogen produce a range of rates of uncatalyzed isomerizations of greater than 14 powers of 10.^{57,61} Attempts to elucidate the mechanisms (lateral shift, rotational, or intermediate possibilities) of individual thermal imine isomerizations continue to challenge the ingenuity of various research groups and provide fuel for controversy.⁶⁴⁻⁷⁰

As part of an ongoing program concerned with the photochemistry of the C-N double bond, we have investigated the solution phase syn-anti photoisomerization of an oxime ether in order to clarify the mechanistic details of the C-N double bond photoisomerization. The great configurational stability of oxime ethers at room temperature stands in striking contrast to the behavior of *N*-aryl- and alkylimines.⁵⁷ These oxime ethers are attractive candidates for mechanistic photostudies since the presence of the methoxyl group drastically reduces the rate of thermal interconversion ($k < 10^{-13}$ at 60°). In the present paper we report on some aspects of the direct and sensitized isomerization of the syn and anti isomers of acetophenone oxime *O*-methyl ether. The results obtained are of fundamental interest by virtue of the superficial parallels to and mechanistic differences from the corresponding situation in olefin photochemistry.

Results

A. Preparation and Properties of Acetophenone Oxime *O*-Methyl Ethers. The *anti-O*-methyl ether of acetophenone oxime (**1**) was synthesized by *O*-methylation of the silver salt of acetophenone oxime (nmr (CCl₄) τ 7.91 (s, 3 H), 6.08 (s, 3 H)).⁷¹ The corresponding syn isomer **2** was prepared by irradiation of **1** in pentane using a 2537-Å source (nmr (CCl₄) τ 7.88 (s, 3 H), 6.25 (s, 3 H)). The two isomers could be readily separated by vapor phase chromatography and their thermal stability was established by heating each



isomer separately at 150° for 168 hr (in benzene) 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 (98% anti and 2% syn oxime ether). The ultraviolet absorption spectra of both the syn and anti forms resembled that of α -methylstyrene. The 0-0 band of the syn isomer appears at 2850 Å (100 kcal/mol) while that of the anti form appears at 2900 Å (98 kcal/mol). These absorptions can be attributed to a π - π^* transition; no absorption corresponding to a lower energy n - π^* transition was observed.

B. Direct Irradiation Experiments. Irradiation of degassed pentane solutions of syn (or anti) oxime ethers (**1** or **2**) at 2537 Å led to a photostationary state ratio (syn/anti) of 2.20 ± 0.03 over a wide concentration range (see Table I). The quantum yield for syn \rightarrow

Table I. Quantum Yields and Photostationary State for the Direct Isomerization of the Syn and Anti Isomers of Acetophenone Oxime *O*-Methyl Ether

Concn, <i>M</i>	$\Phi_{A \rightarrow S}$	$\Phi_{S \rightarrow A}$	$\frac{\Phi_{A \rightarrow S}}{\Phi_{S \rightarrow A}}$	$\frac{[\text{syn}]}{[\text{anti}]_{\text{obsd}}}$	$\frac{[\text{syn}]}{[\text{anti}]_{\text{calcd}}}$
0.29	0.37	0.31	1.19		2.30
0.20				2.17	
0.14	0.35	0.30	1.17		2.26
0.10				2.13	
0.07	0.36	0.29	1.24		2.40
0.05				2.18	
0.03	0.37	0.28	1.32	2.21	2.56
0.01				2.15	

anti isomerization at 2537 Å was 0.29 ± 0.02 in the 4-5% reaction range, while that for anti \rightarrow syn was 0.37 ± 0.02 . The photostationary state obtained in the direct irradiation should be given by the following expression (eq 1).⁷² With the available data,⁷³ the photo-

$$\frac{[\text{syn}]}{[\text{anti}]} = \frac{\epsilon_{\text{anti}}[\Phi_{\text{anti} \rightarrow \text{syn}}]}{\epsilon_{\text{syn}}[\Phi_{\text{syn} \rightarrow \text{anti}}]} \quad (1)$$

stationary state was calculated to be 2.40 ± 0.2 , which is fairly close to the experimental limits of the observed value. It is interesting to note that the direct photoisomerization could not be quenched by high (*ca.* 3 *M*) concentrations of piperylene. This is indicative of reaction from a single state or from the triplet manifold at a rate exceeding diffusional control.

C. Triplet Sensitized Isomerization Experiments. Photoisomerization about the C-N double bond of the oxime ethers (**1** and **2**) could also be induced by triplet excitation. Various sensitizers with known triplet energies were employed to reach a sensitized photo-

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(73) At 2537 Å, $\epsilon_{\text{anti}} 0.982 \times 10^4$ and $\epsilon_{\text{syn}} 0.507 \times 10^4$. The ratio of the extinction coefficients of the syn and anti isomers does not vary significantly with the wavelength of light used. A low-pressure mercury arc (Southern Electric U.V. Co-RPR-2537 Å) lamp was used in these experiments.

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Table II. Photosensitized Isomerization Quantum Yields for the Syn and Anti Oxime Ethers^a

Sensitizer, <i>M</i>	E_T	[Oxime], <i>M</i>	$\Phi_{A \rightarrow S}^{b,c}$	$\Phi_{S \rightarrow A}^{b,c}$	$\Phi_{A \rightarrow S} / \Phi_{S \rightarrow A}$	Φ_{Total}
Propiophenone, 0.05	74.6	0.13	0.37	0.35	1.04	0.72
		0.03	0.37	0.33	1.10	0.70
Acetophenone, 0.04	73.6	0.13	0.36	0.41	0.87	0.77
		0.03	0.37	0.33	1.09	0.70
3-Methoxyacetophenone, 0.03	72.4	0.13	0.36	0.41	0.87	0.77
		0.03	0.36	0.33	1.09	0.69
4-Methoxyacetophenone, 0.03	71.7	0.13	0.32	0.36	0.89	0.68
		0.03	0.31	0.36	0.86	0.67
Benzophenone, 0.04	68.6	0.13	0.32	0.36	0.88	0.68
		0.03	0.31	0.35	0.90	0.66
Triphenylene, 0.005	67	0.01	0.35	0.35	1.0	0.70
Phenanthrene, 0.01	62	0.13	0.28	0.29	0.96	0.57
		0.01	0.28	0.17	1.73	0.45
Naphthalene, 0.07	61	0.13	0.29	0.14	2.05	0.43
		0.01	0.29	0.08	3.55	0.37
2-Acetonaphthone, 0.03	59.3	0.13	0.34	0.06	5.9	0.40
		0.03	0.34	0.04	8.5	0.38
Chrysene, 0.01	57	0.016	0.16	0.013	12.6	0.17
1-Naphthaldehyde, 0.05	56	0.016	0.20	0.028	7.2	0.23
Benzil, 0.02	53.7	0.016	0.008	0.01	0.83	0.02

^a Corrected for back reaction where necessary. ^b Standard deviation ± 0.01 . ^c A 3130-Å source in pentane solvent.

stationary state (see Figure 1). The concentration of the sensitizer was adjusted so that it absorbed >99% of the incident light at 3130 Å. The plot obtained (Figure 1) showed several features comparable to those found in the study of stilbenes,⁷² namely (1) a high-energy region in which the stationary state ratio is *ca.* 1.5, (2) a gradual increase in the syn/anti ratio from 72 down to 59 kcal of triplet energy, and (3) a sharp decrease from 59 down to 54 kcal. The latter two observations can be satisfactorily explained by nonvertical excitation of the acceptor. From Figure 1 we can approximate the triplet energy levels of both isomers as anti ($E_T \sim 59$ kcal) and syn ($E_T \sim 72$ kcal) if we assume that the syn energy level is the cause of the asymptotic behavior of the plot and the anti energy level is located at the maximum syn/anti ratio. More accurate energy level determinations of the triplet spectroscopic states were not possible since both the syn and anti isomers showed no phosphorescence emission.

The quantum yields for the sensitized isomerizations, using a number of different triplet sensitizers, are summarized in Table II. At the oxime ether concentrations used in these experiments (0.016–0.13 *M*), the quantum yields were found to be independent of anti oxime concentration and only slightly dependent on the syn concentration. It is important to note that the predicted photostationary state values (*i.e.*, $\Phi_{A \rightarrow S} / \Phi_{S \rightarrow A}$) in these triplet sensitized experiments are not in agreement with the photostationary state values actually obtained (see Table III). This would suggest that the rate constants for quenching the sensitizer triplets by the two oxime ethers are not the same.

D. Oxime Ethers as Triplet Quenchers. In order to demonstrate that energy transfer to the oxime ethers by sensitizers with $E_T > 72$ kcal does not proceed with identical quenching rates, the relative quenching rates of the syn and anti isomers were determined. This was done by several procedures. In one set of experiments, the relative ability of the syn and anti oxime ethers to quench the phosphorescence emission of acetophenone, benzophenone, naphthalene, and phenanthrene was measured by plotting the intensity of emission *vs.* concentration of the oxime ether (0.01 to 0.1 *M*). The

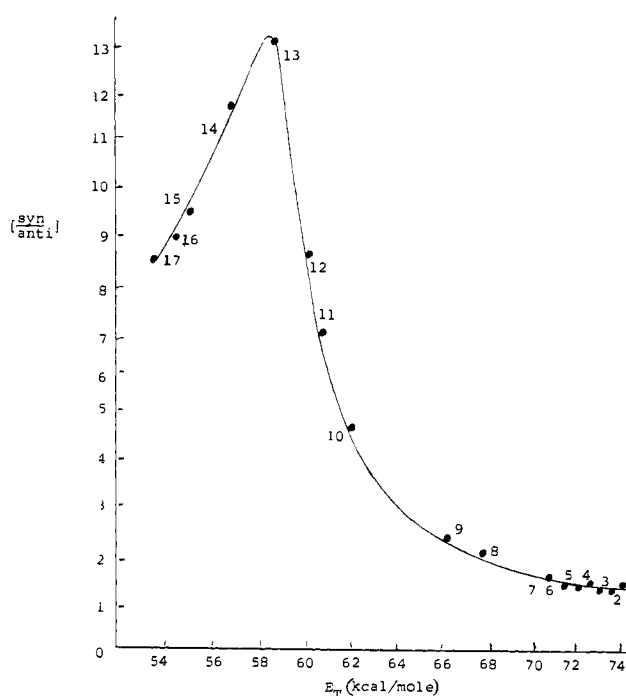


Figure 1. Photostationary state ratios *vs.* energies of triplet sensitizers: (1) propiophenone; (2) xanthone; (3) acetophenone; (4) isobutyrophenone; (5) 3-methoxyacetophenone; (6) benzaldehyde; (7) 4-methoxyacetophenone; (8) benzophenone; (9) triphenylene; (10) phenanthrene; (11) 4-acetylbiphenyl; (12) naphthalene; (13) 2-acetonaphthone; (14) chrysene; (15) 1-naphthaldehyde; (16) biacetyl; (17) benzil.

Table III. Comparison of the Triplet Sensitized Ratio of Quantum Yields and Observed Photostationary States

Sensitizer	E_T , kcal	$[O_S]_{ps}/[O_A]_{ps}$	$\Phi_{A \rightarrow S} / \Phi_{S \rightarrow A}$
Propiophenone	74.6	1.64	1.10
Acetophenone	73.6	1.64	1.09
3-Methoxyacetophenone	72.4	1.65	1.09
4-Methoxyacetophenone	71.7	1.38	0.86
Benzophenone	68.6	2.58	0.90
Phenanthrene	62.0	4.47	1.25
Naphthalene	61.0	8.25	3.55

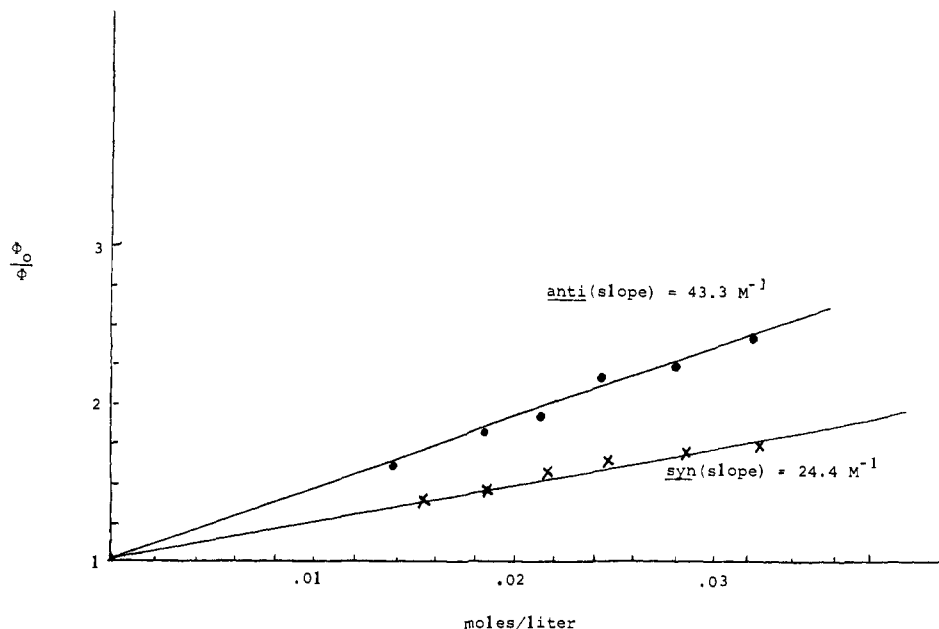


Figure 2. Quenching of the type II photoelimination of valerophenone by oxime ethers.

plots gave reproducible straight lines and the pertinent data from these measurements are summarized in Table IV. The results indicate that the anti isomer quenched

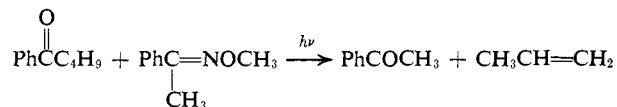
Table IV. Stern-Volmer Slopes for the Quenching of the Phosphorescence of Acetophenone, Benzophenone, Naphthalene, and Phenanthrene by the Oxime Ethers^a

Phosphor (<i>M</i>)	Excitation wavelength, Å	Emission wavelength, Å	Slope, M^{-1}		Slope ratio k_6/k_7
			Syn $k_7\tau$	Anti $k_6\tau$	
Acetophenone (0.1)	3200	4270	14.4	19.2	1.33
Benzophenone (0.1)	3500	4600	11.4	16.2	1.42
Naphthalene (0.1)	3000	5400	1.80	16.8	9.33
Phenanthrene (0.1)	3700	5100	0.5	12.2	24.5

^a In EPA (5:5:2) at 77°K.

the emission of benzophenone and acetophenone approximately 1.3–1.4 times more efficiently than did the syn isomer. The difference in quenching efficiency was observed to be much larger when the emission of naphthalene and phenanthrene was monitored.

To reinforce these low-temperature emission studies, two additional systems were used to compare the quenching efficiencies of the syn and anti isomers. In one case, the relative ability of the oxime ethers to quench the type II cleavage of valerophenone⁷⁴ was studied. A 0.1 *M* solution of valerophenone in pentane

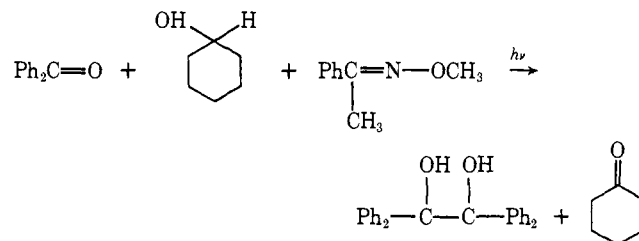


was irradiated at 3130 Å in the presence of the oxime ethers. Typical Stern-Volmer quenching curves were obtained by plotting Φ_0/Φ_q for the Norrish type II reaction *vs.* concentration of the oxime ethers (see Figure 2). The results obtained indicate that the rate of

(74) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

quenching by the anti isomer is approximately 1.8 times faster than the syn isomer.⁷⁵

Another experiment which was designed to measure the relative quenching ability of the oxime ethers was the quenching of the photoreduction of benzophenone in cyclohexanol.



Analysis of the Stern-Volmer quenching slopes ($k_q\tau$) showed that the anti isomer quenched the photoreduction approximately 2.3 times faster than did the syn isomer (see Figure 3). For comparison purposes, the quenching slope of the photoreduction by *trans*-stilbene is also included in Figure 3. In this case the quenching rate for *trans*-stilbene (k_q) is significantly larger than either the syn ($k_q/k_{syn} = 6.2$) or anti ($k_q/k_{anti} = 2.7$) isomer. This observation supports the contention that the oxime ethers quench sensitizer triplets with different rate constants and at values which are less than diffusion control.

E. Double Sensitization Experiments. The observation that piperylene did not quench the syn-anti photoisomerization reaction does not necessarily mean that the direct irradiation proceeds by way of a singlet

(75) From an earlier work of Wagner and Kochevar,⁷⁶ the quenching slope of valerophenone's photoelimination by 2,5-dimethyl-2,4-hexadiene was determined to be $k_q\tau = 95 M^{-1}$. The triplet lifetime (τ) of valerophenone was 7.2×10^{-9} sec and the triplet quenching rate for 2,5-dimethyl-2,4-hexadiene was calculated to be $13.2 \times 10^9 M^{-1} \text{sec}^{-1}$. Using the same lifetime, the quenching rate constants 6.0×10^9 and $3.4 \times 10^9 M^{-1} \text{sec}^{-1}$ were calculated for the anti and syn isomers, respectively. A slight impurity in the solvent or in the ketone could explain the small differences in the quenching slopes observed in the two laboratories (*i.e.*, anti isomer *vs.* 2,5-dimethyl-2,4-hexadiene).

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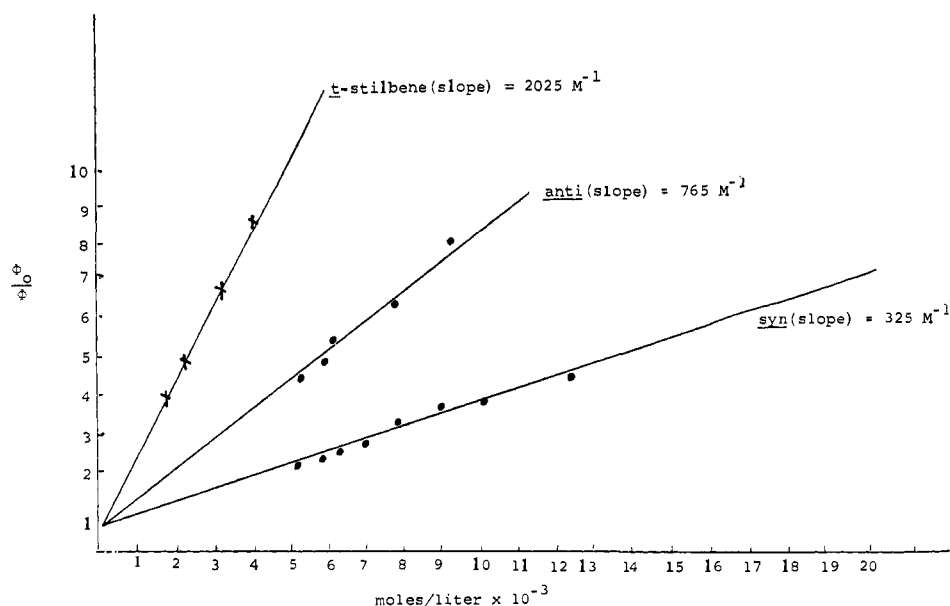


Figure 3. Quenching of the photoreduction of the benzophenone-cyclohexanol system by the oxime ethers and *trans*-stilbene.

state, since a very reactive triplet intermediate which proceeds onto products at a rate faster than diffusional control would also accommodate the data. In an attempt to circumvent this problem, a number of double sensitization experiments were performed where mixtures of *trans*-stilbene ($E_T = 52$ kcal) and the syn ($E_T = 72$ kcal) and anti oxime ($E_T = 59$ kcal) ethers were irradiated in the presence of benzophenone (see Table V)

Table V. Double Sensitization Experiments^a

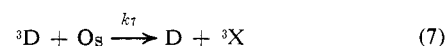
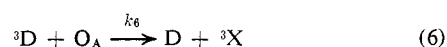
Syn	Anti	Ph ₂ C=O	<i>trans</i> - Stilbene	$\Phi_{S \rightarrow A}$	$\Phi_{A \rightarrow S}$	$\Phi_{I \rightarrow O}$
0.2		0.05		0.40		
0.2		0.05	0.025	0.18		0.28
	0.2	0.05			0.40	
	0.2	0.05	0.025		0.24	0.15
0.10		0.05		0.42		
0.10		0.05	0.025	0.12		0.35
	0.10	0.05			0.39	
	0.10	0.05	0.025		0.23	0.29
0.05		0.05		0.37		
0.05		0.05	0.025	0.07		0.43
	0.05	0.05			0.37	
	0.05	0.05	0.025		0.14	0.34
0.025		0.05		0.34		
0.025		0.05	0.025	0.03		0.46
	0.025	0.05			0.34	
	0.025	0.05	0.025		0.07	0.39
		0.05	0.025			0.45

^a Quantum yields associated with the competitive isomerization of *trans*-stilbene and the syn and anti oxime ethers in the presence of benzophenone.

under conditions where all the light was absorbed by the sensitizer. From the data listed in Table V, it can be seen that *trans*-stilbene is a much more efficient quencher of benzophenone's triplet than either the syn or anti isomer. The significance of these numbers and their bearing on the problem of identifying the multiplicity of the excited state involved in the direct irradiation experiments will be discussed at a later point in this paper.

Discussion

The sensitized syn-anti isomerization of the oxime ethers by a triplet energy donor can be described by eq 2-9.^{7,2} In these equations D, ¹D, and ³D represent



the triplet donor in its ground, excited singlet, and excited triplet states, O_S and O_A represent the syn and anti oxime ether, and ³X represents a twisted oxime ether species. Equation 3 summarizes both radiationless and radiative unimolecular singlet decay. The spectroscopic states of the syn and anti oxime ethers are not included since their conversion to ³X is considered to be fast compared to other processes that might be available to them. The energy transfer depicted by the rate constants k_6 and k_7 includes both classical and nonvertical triplet energy transfer. A kinetic analysis of eq 2-9 leads to the following expressions for quantum efficiencies of pure anti or syn isomers (eq 10 and 11).

$$\Phi_{A \rightarrow S} = \frac{k_4}{k_3 + k_4} \frac{k_6[O_A]}{k_5 + k_6[O_A]} \frac{k_9}{k_8 + k_9} \quad (10)$$

$$\Phi_{S \rightarrow A} = \frac{k_4}{k_3 + k_4} \frac{k_7[O_S]}{k_5 + k_7[O_S]} \frac{k_8}{k_8 + k_9} \quad (11)$$

The three terms on the right side of the equations represent efficiencies of intersystem crossing, energy trans-

fer, and decay with isomerization (decay ratio), respectively. The ratio of the quantum yields is given by eq 12 and the photostationary state is given by eq 13.

$$\frac{\Phi_{A \rightarrow S}}{\Phi_{S \rightarrow A}} = \frac{k_9 k_6 [O_A] k_5 + k_7 [O_S]}{k_8 k_7 [O_S] k_5 + k_6 [O_A]} \quad (12)$$

$$[O_S]_{\text{pss}}/[O_A]_{\text{pss}} = (k_6/k_7)(k_9/k_8) \quad (13)$$

When $[O_S] = [O_A]$, eq 13 transforms into eq 14, where

$$\frac{\Phi_{A \rightarrow S}}{\Phi_{S \rightarrow A}} = \frac{[O_S]_{\text{pss}} k_5 + k_7 [O_S]}{[O_A]_{\text{pss}} k_5 + k_6 [O_A]} \quad (14)$$

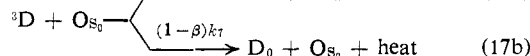
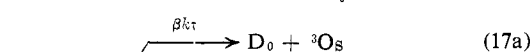
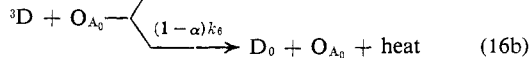
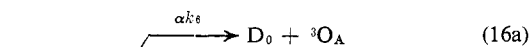
k_5 represents both the radiationless and radiative decay of sensitizer and k_6 and k_7 represent the quenching rate for the anti and syn isomers.

The data outlined in the Results section clearly indicate that the rate constants for quenching high-energy triplet sensitizers by the two oxime ethers are not the same. This difference is undoubtedly responsible for the poor correlation of the observed photostationary state values with the ratio of the triplet sensitized quantum yields (see Table III). Consideration of the data in Table II shows that at the oxime ether concentrations used in these experiments, Φ is more or less independent of oxime ether concentration and thus $k_5 \ll k_6 [O_A]$ and $k_7 [O_S]$. Since the quantum efficiencies were determined at identical oxime ether concentrations, eq 14 can best be approximated by eq 15. The "excitation ratio"

$$[O_S]_{\text{pss}}/[O_A]_{\text{pss}} = \frac{\Phi_{A \rightarrow S} k_6}{\Phi_{S \rightarrow A} k_7} \quad (15)$$

k_6/k_7 obtained with high-triplet sensitizers is $ca. 1.60 \pm 0.1$ (the anti isomer is a better triplet acceptor than the syn form) while the "decay ratio" is 1.0 ± 0.1 . The deviation of the excitation ratio from unity appears to be a consequence of the fact that energy transfer from the high-triplet sensitizers to the syn isomer is not yet diffusion controlled.

The gradual increase in the value of $(\text{syn/anti})_{\text{pss}}$ when the triplet energy level of the sensitizer drops from 72 to 59 kcal (see Figure 1) can also be related to the nonidentity of the quenching rates (*i.e.*, $k_6 \neq k_7$). As the sensitizer energy is varied between 72 and 59 kcal, a rapid falloff in transfer rate to the syn isomer is expected, thus pumping the system to higher $(\text{syn/anti})_{\text{pss}}$ values. The fact that the sum of the triplet sensitized quantum yields, $\Phi_{S \rightarrow A} + \Phi_{A \rightarrow S}$, is less than unity, even when high-energy sensitizers are used (see Table II), suggests that the triplet states of the oxime ethers include radiationless decay processes which proceed by paths not involving syn-anti isomerization. Alternatively, the inefficiency encountered with the sensitized experiments may indicate that not all high-energy sensitizers are effective in generating a twisted imine triplet. This is probably the result of energy wastage during the triplet quenching process and is illustrated by eq 16 and 17 where α and β represent partitioning



factors. Energy wastage in the photosensitized isomerization of stilbenes has been reported by Hammond and Valentine⁷⁷ and provides good analogy for the above suggestion. Consequently, the deviation of the "excitation ratio" (k_6/k_7) in the above system can be attributed to both the difference in quenching rates and quenching efficiencies.

An additional factor which would be expected to influence the "excitation ratio" and consequently affect the slope of Figure 1 is "nonvertical energy transfer."⁷² In the 59–72-kcal region, the syn isomer cannot accept energy by a classical triplet energy transfer step since the assigned spectroscopic energy level of the syn isomer (*ca.* 72 kcal) is above that of the triplet sensitizers used. The photoisomerization of the syn to the anti isomer must then proceed by endothermic energy transfer. Consequently, as the sensitizer energy is varied between 72 and 58 kcal, a falloff in transfer rate (k_7) to the syn isomer occurs (nonvertical energy transfer) while k_6 remains relatively constant. As the sensitizer energy drops below 59 kcal, the photostationary state ratio $((\text{syn/anti})_{\text{pss}})$ and total quantum efficiency decrease drastically. At this point, the rates of energy transfer have simply become slower than the decay rates of the sensitizer.

The data that we have obtained clearly indicate that the syn-anti isomerization of the oxime ethers can be induced by direct irradiation as well as by triplet sensitization. If decay from a common twisted state is involved in the sensitized and unsensitized experiments, the photostationary state derived from direct irradiation should be related to that obtained with high-energy sensitizers in the following way

$$\frac{[\text{anti}]}{[\text{syn}]} = \frac{\epsilon_{\text{anti}} [\Phi_{\text{anti} \rightarrow \text{syn}}]_s}{\epsilon_{\text{syn}} [\Phi_{\text{syn} \rightarrow \text{anti}}]_s} \quad (18)$$

This relationship predicts a photostationary state of $\text{syn/anti} = 2.10 \pm 0.2$ for propiophenone and acetophenone and 1.66 ± 0.1 for *p*-methoxyacetophenone. The calculated photostationary state values are greater than the observed values by a factor of *ca.* 1.3. We have already shown that the sensitized quantum yield ratio is not related to just the decay ratio but also depends on the excitation ratio. Consequently, we cannot use eq 18 to demonstrate the nature of the excited state in the direct irradiation experiments.

The observation that piperylene did not quench the syn-anti photoisomerization does not necessarily mean that the direct irradiation proceeds by way of a singlet state, since a very reactive triplet intermediate which proceeds onto products at a rate faster than diffusional control would also accommodate the data. From the data listed in Table V, it can be seen that *trans*-stilbene is a much more efficient quencher of benzophenone's triplet than either the syn or anti isomer. This had already been demonstrated by quenching the benzophenone-cyclohexanol photoreduction (see Figure 3). As was noted earlier, the triplet quenching rate associated with *trans*-stilbene (k_q) is significantly larger than either the syn ($k_q/k_7 = 6.2$) or anti ($k_q/k_6 = 2.7$) isomer. The double sensitization experiment, which was carried out at equal concentrations of *trans*-stilbene and oxime ether, is most informative and bears discussion.

(77) D. Valentine, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3449 (1972).

Under these conditions, the *trans*- → *cis*-stilbene $\Phi = 0.39$ while the *syn* → *anti* $\Phi = 0.07$. When the *syn* oxime ether is used, the *trans*- → *cis*-stilbene $\Phi = 0.46$ while *syn* → *anti* $\Phi = 0.03$. The quantum yield of the benzophenone sensitized isomerization of *trans*-stilbene has a value of 0.45 while that of the benzophenone sensitized isomerization of the *syn* or *anti* oxime ether is 0.34. In the double sensitization experiment, the ratio of $\Phi_{t \rightarrow c}/\Phi_{A \rightarrow S} = 5.6$ whereas $\Phi_{t \rightarrow c}/\Phi_{S \rightarrow A} = 15.3$ (see Table VI). We have already obtained the relative

Table VI. Comparative Study of the Competitive *vs.* Noncompetitive Quenching of the Triplet State of Benzophenone

Competitive Φ	Noncompetitive Φ	Com- petitive $\Phi_{t \rightarrow c}/\Phi$	k_q/k_6	k_q/k_7	Noncom- petitive $0.45/\Phi$
$\Phi_{t \rightarrow c} = 0.39$	$\Phi_{t \rightarrow c} = 0.45$	1	2.67		1
$\Phi_{A \rightarrow S} = 0.07$	$\Phi_{A \rightarrow S} = 0.34$	5.6			1.32
$\Phi_{t \rightarrow c} = 0.46$	$\Phi_{t \rightarrow c} = 0.45$	1		6.25	1
$\Phi_{S \rightarrow A} = 0.03$	$\Phi_{S \rightarrow A} = 0.34$	15.3			1.32

quenching rates of *trans*-stilbene and the *syn* and *anti* oxime ethers by determining the quenching slopes of the photoreduction of benzophenone in cyclohexanol. From this experiment, the product of the quantum yield and excitation ratios should reflect the competitive ratio of the quantum yields in the double sensitization experiment (*i.e.*, eq 19). In this expression $\Phi = \Phi_{A \rightarrow S}$ or

$$\left[\frac{\Phi_{t \rightarrow c}}{\Phi} \right]_{ds} \approx \left[\frac{0.45 k_q}{\Phi k} \right]_p \quad (19)$$

$\Phi_{S \rightarrow A}$, $0.45 = \Phi_{t \rightarrow c}$ stilbene, k_q = quenching rate of *trans*-stilbene, $k = k_6$ or k_7 , *ds* = double sensitization (competitive) experiment, and *p* = photoreduction experiment of benzophenone in cyclohexanol. The actual values obtained are given in Table VII. The competitive

Table VII. Results Obtained from the Utilization of Equation 19

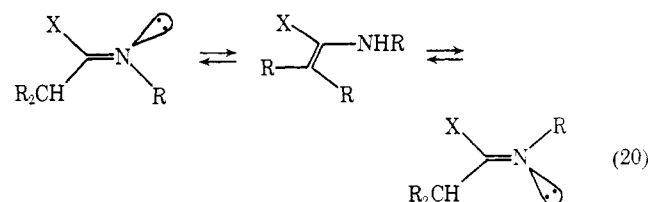
Φ	k	$[\Phi_{t \rightarrow c}/\Phi]_{ds}$	$\left[\frac{0.45 k_q}{\Phi k} \right]_p$
$\Phi_{A \rightarrow S}$	k_6	5.6	3.5
$\Phi_{S \rightarrow A}$	k_7	15.3	8.3

quantum yield ratios are larger than the predicted ones by a factor of 1.6–1.8. The difference between the two sets of numbers suggests that the energy transferred from benzophenone to the oxime ether is, in turn, being transferred on to stilbene. It is well known that *trans*-stilbene can accept energy from triplet sensitizers.⁷² Since *trans*-stilbene has a lower triplet excitation energy than either the *syn* or *anti* oxime ether, there is a good possibility that a certain amount of triplet energy transfer occurs from the oxime ethers to *trans*-stilbene before the oxime ethers have a chance to isomerize. This would account for the discrepancy in the competitive and noncompetitive experiments described above. If this is the case, then it is clear that the triplet photoisomerization cannot proceed at a rate which is faster than diffusion controlled. Consequently, one should have been able to quench the photoisomerization of the oxime ethers with piperylene if a triplet state was involved in the direct irradiation. Since the reaction was not quenchable and did not result in the isomeriza-

tion of piperylene, it follows that the reactive state involved in the direct irradiation is an electronically excited singlet state.

It is also interesting to note that the sum of the quantum yields, $\Phi_{S \rightarrow A} + \Phi_{A \rightarrow S}$, in the direct irradiation (see Table I) is less than unity. This suggests that deactivation of the singlet state of the oxime ethers includes radiationless decay processes which proceed by paths not involving *syn*-*anti* isomerization. The source of inefficiency may be related to energy-degrading processes within a twisted excited state or may possibly involve relaxation of planar excited states in competition with decay of the twisted form. Although radiationless paths which maintain geometric integrity are important to a degree, *syn*-*anti* isomerization provides the major route for deactivation of the excited imine state.

The mechanism of interconversion of imine diastereomers in the ground state is the subject of considerable debate^{78–80} and has been considered in terms of either a planar inversion mechanism or a rotation mechanism, with the latter probably involving a dipolar transition state. In addition to the two intramolecular mechanisms, a third mechanism has been proposed for imines which contain a C-alkyl substituent with at least one α -hydrogen atom.⁸¹ The interconversion of (*Z*-) and (*E*-)imines of this type could proceed by tautomerization of the imine to an enamine (eq 20). Our work



on the photoisomerization of the *syn* and *anti* oxime ethers (1 and 2) led us to consider whether the photoisomerization process could proceed by a photochemically induced 1,3-sigmatropic hydrogen shift. Such a process (eq 20) would be allowed in the excited state and consequently merits attention. Irradiation of the *syn* or *anti* oxime ether in deuteriomethanol produced the same photostationary state as was obtained in pentane. Examination of the nmr spectrum showed that the photoisomerization proceeded without deuteration of the C-methyl group. This observation clearly demonstrates the absence of an oxime ether-enamine mechanism for the *syn*-*anti* photoisomerization process.

The mechanism by which the *syn* and *anti* isomers are interconverted in the excited state is not known. Whether isomerization about the C–N double bond proceeds by rotation or linear inversion remains to be clarified. It has not been the purpose here to try to examine the mechanism of interconversion or to determine the possible type of electronic states (π - π^* or n - π^*) involved in the isomerization but only to point out some general features which the data seem to imply.

(78) For recent reviews, see J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970).

(79) I. O. Sutherland, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, **4**, 71 (1971).

(80) C. G. McCarty in "The Chemistry of the Carbon-Nitrogen Double Bond," S. Patai, Ed., Interscience, London, 1969, p 363.

(81) W. B. Jennings and D. R. Boyd, *J. Amer. Chem. Soc.*, **94**, 7187 (1972).

It should be noted, however, that the only excited states of imines which should decrease in energy as rotation is carried out about the C–N double bond are the π – π^* states; the n – π^* states should retain considerable double bond character and so should offer significant resistance to rotation. This might also account for the inefficiency observed in the direct photoisomerization.

Experimental Section

syn- and anti-O-Methyl Ethers of Acetophenone Oxime. A 13.5-g sample of acetophenone oxime in 100 ml of anhydrous ether was slowly added to a suspension of sodium methylate (5.4 g) in anhydrous ether. The sodium salt of the acetophenone oxime precipitated from the solution. The precipitate was filtered and then dissolved in 100 ml of distilled water. To this mixture was added a saturated aqueous silver nitrate solution until the dark brown silver salt had completely precipitated. The silver salt was filtered and was taken up in ether. To this suspension was added 67 g of methyl iodide at 0° and the mixture was allowed to stir for 3 hr in the ice bath. After this time the mixture was filtered to remove silver iodide and the solution was dried over magnesium sulfate. The solvent was removed under reduced pressure to give 14.0 g (94%) of a yellow oil. Analysis of the oil by glpc using a 0.25 in. \times 10 ft copper column packed with 10% FS-1265 on Diasaport S at 150° revealed that the oil contained 3–5% of the acetophenone, 2% of the syn isomer, and 95% of the anti-O-methyl ether of acetophenone oxime (1). The small amount of acetophenone present was removed by treating the oil with Girard's T reagent.⁸² A 1.0-g sample of Girard's T reagent in 10 ml of 1:1 ethanol–glacial acetic acid was prepared. To this solution was added 1.0 g of the above yellow oil and the mixture was heated to 100° for 10 min. After cooling to room temperature, the mixture was added to 10 ml of water and then extracted with ether. The ethereal solution was dried over magnesium sulfate and the solvent was removed under reduced pressure. This procedure was repeated until glpc analysis revealed the complete absence of acetophenone. The residual oil was then distilled at 54–60° (0.5 mm) to give pure anti oxime ether (1): ir (neat) 3.42, 6.24, 6.95, 7.32, 7.65, 9.55, 11.20, 13.15, and 14.50 μ ; uv (cyclohexane) 248 nm (ϵ 10,990); nmr (CCl₄) δ 3.92 (3 H, s), 2.12 (3 H, s), and 7.6 (5 H, m);⁷¹ m/e (70 eV) 149 (M⁺), 134, 119, 118, 108, 103, and 77 (P).

The corresponding syn oxime ether (2) was prepared by irradiating the anti isomer in pentane at 2537 Å. The mixture of isomers was separated by thick-layer chromatography using a 9:1 benzene–ethyl acetate mixture as the eluent. The syn isomer was further purified by distillation at 65–70° (10 mm). The purity of the syn isomer was established by glpc analysis: ir (neat) 3.42, 3.60, 6.20, 6.71, 6.85, 6.95, 7.29, 9.05, 9.51, 11.18, 13.10, and 14.50 μ ; uv (cyclohexane) 238 nm (ϵ 6080); nmr (CCl₄) δ 2.09 (3 H, s), 3.75 (3 H, s), and 7.6 (5 H, m);⁷¹ m/e (70 eV) 149 (M⁺), 134, 119, 118, 108, 103, and 77 (P).

Determination of Photostationary States for Oxime Ether Isomerizations. A. Direct Irradiation. Solutions containing the substrate at a fixed concentration in a chosen solvent were irradiated through quartz tubes at 2537 Å. All samples were degassed using a vacuum line which achieved a pressure of $<5 \times 10^{-4}$ mm. Three freeze–thaw cycles were used with cooling in liquid nitrogen. Irradiation of samples were carried out using a Model PRP-100 Rayonet photochemical reactor with a motor-driven “merry-go-round” turntable. Analyses of the photostationary compositions were carried out using standard glpc techniques. The photostationary state values were obtained by irradiating the pure oxime ethers (syn or anti) until both had reached a constant photostationary state value.

B. Sensitized Photostationary States. Solutions containing the sensitizer and substrate at a fixed concentration in a chosen solvent were irradiated through Pyrex culture tubes at 3130 and 3660 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.⁸³ The 3660-Å mercury line was isolated by Corning filters CS 7-37 and CS 0-52 placed in series.⁷² 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 at 1-day intervals in the irradiation to ensure that the actual stationary composition had been reached. Preliminary experiments were run with inefficient sensitizers in order to obtain an approximate value of the photostationary state. The photostationary state value was then bracketed by preparing two isomeric solutions that were greater and less in value in comparison to the preliminary photostationary state ratio. This permitted shorter irradiation times to be used and consequently eliminated extensive problems associated with long irradiation times. In every case investigated, the average values of two steady state determinations differed by less than the measured uncertainty in either value.

Quantum Yield Determinations. Solutions were prepared in various solvents as described in the Results section, and 3.0 ml of each was placed in separate Pyrex culture or quartz tubes (13 \times 100 mm). Each sample was degassed three times to 0.005 mm and sealed *in vacuo*. In a given run all tubes were irradiated in parallel for the same length of time on a “merry-go-round” apparatus which assured that each sample absorbed the same intensity of light. Benzophenone–benzhydrol⁸⁴ or cyclopentanone⁸⁵ 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 150°. 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 10% or less. The mass balance in these runs was generally better than 98%.

Quenching of the Type II Photoelimination of Valerophenone by the Syn and Anti Oxime Ethers. These quenching studies parallel the experiments of Wagner⁷⁶ who measured the Stern–Volmer quenching slopes for the type II photoelimination of valerophenone with 2,5-dimethyl-2,4-hexadiene. A 0.1 *M* solution of valerophenone in pentane was irradiated with 3130-Å light using degassed Pyrex culture tubes with varying concentrations of the oxime ethers. The solutions were irradiated to less than 0.01% conversion and the per cent of oxime ether isomerization was kept below 10%. The quantum yield for photoelimination was determined by measuring the amount of acetophenone formed. The light intensity was determined during photolysis by benzophenone–benzhydrol actinometry.

Quenching of the Benzophenone–Cyclohexanol Photoreduction by the Syn and Anti Oxime Ethers. Degassed pentane solutions of benzophenone (0.1 *M*) and cyclohexanol (0.1 *M*) were irradiated in Pyrex culture tubes using 3660-Å light with varying concentrations of the syn or anti oxime ether or with *trans*-stilbene. The solutions were irradiated to less than 6% conversion while the photoisomerization of the oxime ether was kept to $<10\%$. The quantum yields for the photoreduction were measured by determining the amount of cyclohexanone formed. The irradiations were carried out in the “quantum yield merry-go-round” which ensured equivalent radiation of each sample. To simplify calculations and permit accurate, direct comparisons of results, as many determinations as possible were carried out at one time. Checks were run to ensure that the values so obtained allowed repetition.

Competitive Quenching of Benzophenone's Triplet by *trans*-Stilbene and the Syn and Anti Oxime Ethers. Degassed solutions of benzophenone (0.05 *M*) in pentane containing varying quantities of a mixture of syn or anti oxime ether with *trans*-stilbene were irradiated at 3660 Å. For measurement of quantum yields for the sensitized reaction alone, the irradiation was carried out with a 450-W Hanovia medium-pressure lamp through Corning 737 and 052 filters. This filter system admits only a narrow band of light of wavelengths equal to 365 ± 5 nm and has been described elsewhere.⁷² All quantum yields were corrected for slight back-reaction. The light intensity was determined during photolysis by benzophenone–benzhydrol actinometry. Hexadecane was used as the internal standard for these measurements.

Phosphorescence Emission Studies. The emission spectra were made on an Aminco-Bowman spectrophotofluorometer with phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. All emission spectra were recorded using EPA (diethyl ether–isopentane–

(82) D. J. Pasto and C. R. Johnson, “Organic Structure Determination,” Prentice-Hall, Englewood Cliffs, N. J., 1969, p 393.

(83) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 1318 (1970).

(84) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).

(85) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970).

ethanol, 5:5:2 volume ratio) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. All phosphorescence samples were degassed by several freeze-thaw cycles. Phosphorescence intensities with or without quencher were reproducible for different samples prepared from the same solution.

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A Possible Photochemical ($\pi 4_s + \pi 2_a$) Diels-Alder Reaction. The Photodimerization of 6,6-Dimethyl-2,3-benzo-2,4-cycloheptadienone

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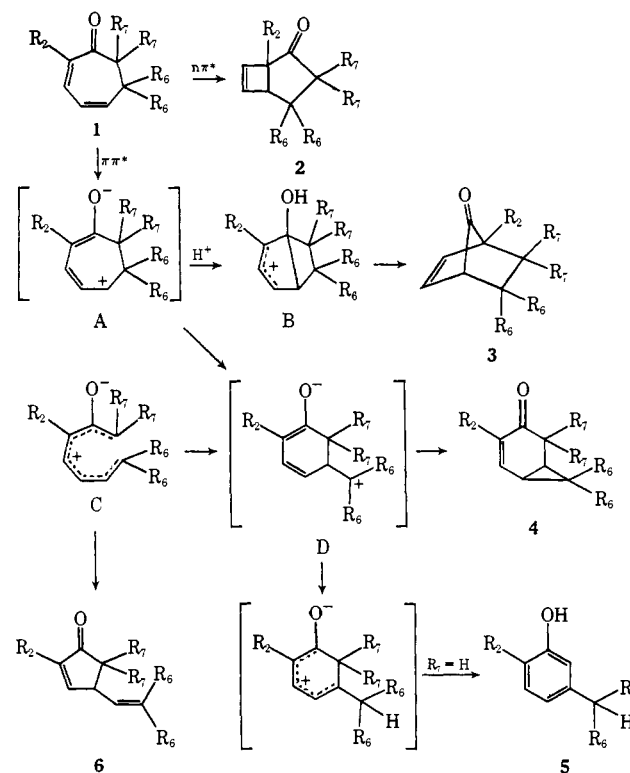
Abstract: Irradiation of the title compound **11** gave predominantly two stereoisomeric dimers, shown by chemical and X-ray crystal data to have the structures **16** and **17**, together with a small amount of a cyclobutane dimer (**19**?). A mechanism which rationalizes the major products involves the cycloaddition of the 4,5 double bond of one monomer unit to the styrene moiety of a second (structures E and F) to give intermediates G and H, followed by a 1,3-acyl shift to permit rearomatization. The major products have four chiral centers, yet only two diastereomers are formed. A preferred mechanism which explains the unique observed stereochemistry requires the cycloaddition to be antarafacial at the 4,5 double bond and suprafacial in the styrene moiety, with the 1,3-acyl shift suprafacial.

The Diels-Alder reaction is well known to occur by a ($\pi 4_s + \pi 2_s$) mechanism, although the possibility for a reaction antarafacial in both components also exists. To conserve orbital symmetry, a concerted *photochemical* Diels-Alder reaction would have to be suprafacial in one component and antarafacial in the other. The major obstacle to observing this reaction path experimentally is the much more accessible allowed photochemical ($\pi 2_s + \pi 2_s$) process. Consequently, intermolecular examples of the photochemical Diels-Alder reaction are rare or unknown. We wish to describe here a photodimerization which may proceed by this path. It was discovered accidentally in the following way.

The photoisomerization of 2,4-cycloheptadienones **1** leads to an exceptional variety of products (**2-6**) whose particular structures depend upon the substitution pattern, solvent polarity, acidity, and excitation wavelength. Scheme I¹ summarizes in a general way the structural changes which occur when 2,4-cycloheptadienones are irradiated, although it is an oversimplification which may require elaboration and modification as more is learned about mechanistic details.

Excitation of **1** to an $n\pi^*$ state in a neutral medium leads to a bicyclo[3.2.0]hept-6-en-2-one (**2**);² singlet and triplet excited states have been implicated.³ In the presence of acid either the excited state of the ketone

Scheme I



(1) H. Hart, *Pure Appl. Chem.*, **33**, 247 (1973).

(2) (a) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 443 (1960); (b) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961); O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962); (c) L. A. Paquette and O. Cox, *ibid.*, **89**, 5633 (1967); (d) K. E. Hine and R. F. Childs, *J. Chem. Soc. D*, 145 (1972); (e) D. I. Schuster and M. A. Tainsky, *Mol. Photochem.*, **4**, 437 (1972).

(3) D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.*, 1657 (1970).

may become protonated or the ketone may be protonated prior to excitation; the sequence is not always clear and certainly depends in part on the acidity of the medium. It is also possible that polar media may lower the energy of the $\pi\pi^*$ state relative to that of the $n\pi^*$ state without protonation. Whatever the details, all the remaining products can be rationalized as stemming