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Differentiation in Singlet Oxygenation Rates of 2,3-Diaryl-2-butenes as a Function of Cis–Trans Isomerism[1]

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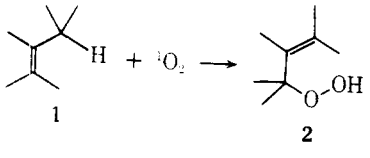
The photosensitized singlet oxygenation of *cis*- and *trans*-2,3-diaryl-2-butenes, including the 2,3-diphenyl (**1a**), 2,3-di-β-naphthyl (**1b**), and 2,3-di-α-naphthyl (**1c**) derivatives, was undertaken. The corresponding 2,3-diaryl-3-hydroperoxy-1-butenes **2a–c** were obtained in essentially quantitative yield and their structures confirmed by iodometry and ^{1}H NMR and IR spectral data. Relative singlet oxygenation rates show that for all cis–trans isomer pairs the cis isomer undergoes ene reaction ca. ninefold faster than the corresponding trans isomer. The greater singlet oxygenation reactivity of the cis isomer in each cis–trans pair correlates well with the first ionization potentials determined by photoelectron spectroscopy in that the more reactive cis isomer has the lower IP (~0.20 eV) for each cis–trans pair. These results are rationalized in terms of the higher steric strain for the more crowded cis isomer.

The chemistry of singlet oxygenation is now well defined, although numerous mechanistic aspects still remain to be resolved in order to understand the details of this important reaction.[3] This applies especially to the classical ene reaction (eq 1) in which an olefinic substrate **1** bearing allylic hydrogens



1 2 (1)

is converted into an allylic hydroperoxide **2**. For example, a recent paper accentuates the substrate reactivity problem by determining the rates of the ene singlet oxygenation of a large collection of diverse alkenes.[4] Thus, the greater the degree of alkylation of the ethylenic bond, the faster the rate of singlet oxygenation, correlating satisfactorily with the lower ionization potentials of the more alkylated substrates.[5] However, the situation is more complex since steric, conformational,[3,6] and ring-strain factors[7] play important roles.

We have been interested in preparing allylic hydroperoxides **2** without allylic hydrogens in order to cycloperoxymercurate them to the corresponding mercury-substituted 1,2-dioxetanes **3**.[8] For this purpose we decided to singlet oxygenate cis–trans mixtures of 2,3-diphenyl-2-butenes **1a** to prepare the desired allylic hydroperoxides **2a**. Much to our surprise we observed that *cis*-2,3-diphenyl-2-butene (**1a**) reacted much faster with singlet oxygen than the trans isomer. To the best of our knowledge only limited and inconclusive data have been reported[10] on the relative reactivity of cis–trans isomers toward singlet oxygen.

It was, therefore, of interest to determine the generality and the factors that influence this novel effect.

Results and Discussion

Besides the cis–trans isomers of 2,3-diphenyl-2-butene (**1a**), we investigated the singlet oxygenation of 2,3-di-α-naphthyl- and 2,3-di-β-naphthyl-2-butenes, respectively **1b** and **1c**. These olefins were prepared by the titanium trichloride–lithium aluminum hydride coupling reaction of the corresponding aryl methyl ketones.[9] Separation into the pure cis and trans isomers was achieved by means of repetitive dry column chromatography on silica gel. The unknown α-naphthyl and β-naphthyl systems were characterized on the basis of elemental analysis, mass spectra, and IR and NMR spectral data. The results are summarized in Table I.

Photosensitized oxygenation of the isomerically pure 2-butenes **1** in CCl_4 and tetraphenylporphyrin (TPP) as sensitizer afforded the corresponding allylic hydroperoxides **2** in essentially quantitative yield. These unknown substances exhibited the characteristic ^{1}H-NMR and IR spectra. Iodometric titration indicated higher than 95% purity. The results are summarized in Table II. It proved difficult to isolate these highly sensitive hydroperoxides since evaporation of the solvent even at subambient temperatures induced rearrangement and decomposition.

The relative singlet oxygenation rates were determined as described previously[10] by following the consumption of the 2-butene **1** substrate and/or the appearance of the hydroperoxide product **2** in the ^{1}H NMR, using the competition technique. For the most reactive substrate, *cis*-**1a**, we employed tetramethylethylene (TME) and for the least reactive, *trans*-**1c**, cyclooctene as internal standard. The remaining substrates were run against each other, i.e., always in pairs in descending order of the reactivity scale. Fortunately the methyl resonances of the substrate, product, and standard and the vinyl resonances of the product and standard were well

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Table I. Yields, Physical Constants, and Spectral Data of *cis*- and *trans*-2,3-Diaryl-2-butenes 1

	registry no.	yield, %	mp, °C	^{1}H NMR (CCl_4) type[a]	H no.	δ	multiplicity	IR (CCl_4), cm^{-1}	MS m/e, eV
cis-**1a**	782-05-8	27	66 (lit.[b] 66–67)	CH_3	3	2.12	s	3080, 3060, 3030, 2930	
				Ph	5	6.85	s (broad)	2860, 1600, 1490, 1375	
trans-**1a**	782-06-9	24	106–107 (lit.[c] 107)	CH_3	3	1.85	s	3080, 3060, 3030, 2930	
				Ph	5	7.14	s (broad)	2860, 1378, 1600, 1490	
cis-**1b**	68797-28-4	44	98–99[d]	CH_3	3	2.28[e]	s	3060, 3020, 2960, 2920	308, 293
				β-Naph	7	7.15	m	2860, 1378, 1600, 1490	278, 166
trans-**1b**	68781-49-7	29	147[d]	CH_3	3	1.96[e]	s	3060, 3020, 2960, 2920	308, 293
				β-Naph	7	7.43	m	2860, 1600, 1382, 1500	178, 165
cis-**1c**	68781-50-0	33	138–140[d]	CH_3	3	2.03[e]	s	3060, 1592, 2920, 2860	308, 278
				α-Naph	7	7.05	m	1580, 1507, 1450, 1380	166
trans-**1c**	68781-51-1	27	202–204[d]	CH_3	3	1.67[e]	s	3060, 2918, 1593, 1580	308, 293
				α-Naph	7	7.4	m	1507, 1450, 1374	278

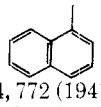
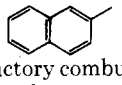
[a] α-Naph =  ; β-Naph =  . [b] A. Mustafa, *J. Am. Chem. Soc.*, **71**, 1878 (1949). [c] I. Wessely and H. Welleba, *Chem. Ber.*, **74**, 772 (1941). [d] Satisfactory combustion analytical data for C,H (± 0.4%) were provided for these compounds. [e] Assignments were made relative to *cis*-**1a** and *trans*-**1a**, for which the CH_3 resonance of the trans isomer was shifted upfield from that of the cis isomer.

Table II. Spectral Data of 2,3-Diaryl-3-hydroperoxy-1-butenes 2

3-hydroperoxy-1-butenes (2)[a,b]	registry no.	purity, %[c]	^{1}H NMR (CCl_4)[d] type	H no.	δ	Multiplicity	IR (CCl_4), cm^{-1}
2a	40188-25-8	94.8	CH_3	3	1.73	s	3500, 3075, 3050, 3025
			CH_2=	2	5.32	s	2990, 2930, 2860
			Ph	10	7.05	m	1620, 1600, 1495
2b	68781-52-2	95.9	CH_3	3	1.77	s	3500, 3050, 2990
			CH_2=	2	5.32	s	2930, 1625, 1590
			β-Naph	14	7.30	m	1495, 880
2c	68781-53-3	98.2	CH_3	3	1.86	s	3490, 3030, 2980
			CH_2=	1	5.21	s	2920, 1625, 1600
				1	5.61	m	1510, 1390, 920
			α-Naph	14	7.50	m	

[a] For the meaning of α-Naph and β-Naph see footnote *a* in Table I. [b] Too unstable to be isolated. [c] Iodometry. [d] The hydroperoxy proton is buried in the aromatic region.

Table III. Relative Singlet Oxygenation Rates and Ionization Potentials of 2,3-Diaryl-2-butenes 1

2-butene	singlet oxygenation rates[a] rel rates	ratio	1st vertical IP, eV[b] $I_{V,1}$	ΔI[c]
cis-**1a**	194		8.00	
trans-**1a**	21.6	9.0	8.26	0.26
cis-**1b**	184		7.50	
trans-**1b**	20.3	9.1	7.76	0.26
cis-**1c**	9.4		7.62	
trans-**1c**	1.0	9.4	7.80	0.18

[a] Tetramethylethylene as internal standard; corrected for statistical factor; within ±5%. [b] Within ±0.02 eV. [c] Difference in IP's between trans and cis isomers.

resolved to permit relative integration of these signals for the determination of the relative rate factors. Appropriate statistical correction for the relative number of protons under the respective integrated signals was made for each competition experiment. The results are displayed in Table III. Also listed are the first vertical ionization potentials for each substrate, determined by photoelectron spectroscopy.

The general trend in singlet oxygenation reactivity is clearly evident in Table III. Without exception the cis isomer of the diphenyl, di-β-naphthyl, and di-α-naphthyl systems, respectively **1a**, **1b**, and **1c**, are ca. ninefold more reactive than the corresponding trans isomers. Furthermore, for each cis–trans pair the ionization potentials of the cis isomer are ca. 5 kcal/mol lower than for the trans isomer. In other words, within each cis–trans pair the cis isomer undergoes ene singlet oxygenation signficantly faster than the trans isomer since its ionization potential is lower. Presumably the transition state for the ene reaction with $^1O_2$ resembles structurally the starting alkene[6] and charge transfer interactions between alkene and $^1O_2$ appear to be significant.[3c,5]

As to why the cis isomers **1a–c** have lower IP's and thus greater ene reactivity toward $^1O_2$ we can only speculate. It is expected that the steric strain in the cis isomer is greater than for the trans isomer for each cis–trans pair. This in turn imparts a greater twisting action around the ethylenic bond to relieve the steric strain. Consequently, the cis substrate is of higher energy content and the HOMO lies at higher energy than for the trans substrate. Therefore, the ionization potential should be lower and the ene reactivity higher.

Unfortunately, other factors such as steric hindrance and conformational effects must also play a significant role in the singlet oxygenation reactivity of these alkenes. For example, the relative rates only correlate well on an intrasubstrate basis, i.e., cis vs. trans for a particular substrate system, but not on

an intersubstrate basis, i.e., phenyl (**1a**), β-naphthyl (**1b**), and α-naphthyl (**1c**). For example, in view of the IP's the intersubstrate $^1O_2$ reactivity should have been Ph < α-Naph ≤ β-Naph, ignoring any differentiation among cis–trans isomers. Clearly, substituent effects on the aryl group of the 2-butenes, especially in the ortho and para positions, will be necessary for the phenyl and naphthyl systems to unravel all the details of this process. However, our observation that ene reactivity of stilbene-type olefins with singlet oxygen depends on geometrical isomerism is significant.

Experimental Section

Melting points are uncorrected. All solvents, reagents, and starting materials were purchased from standard sources and purified according to literature procedures to match reported physical constants. Elemental analyses were performed by Atlantic Analytical Laboratories, Atlanta, Ga. Infrared spectra were taken either on a Perkin-Elmer Infra 237B or Model 283 spectrophotometers, ^{1}H-NMR on a Perkin-Elmer R-24B spectrometer, and mass spectra on a Perkin-Elmer RMS-4 instrument. The photon electron spectra were recorded on a PS 18 photon electron spectrometer (Perkin-Elmer Ltd.), equipped with a heated probe. The samples were heated at 130 °C and calibrated with Ar.

General Preparation of 2,3-Diaryl-2-butenes 1. A 3000-mL, three-necked, round-bottomed flask, equipped with an N_2 inlet and outlet tube, the latter protected with a $CaCl_2$ drying tube, was charged with 37.9 g (0.25 mol) of $TiCl_3$ and 4.2 g (0.11 mol) of $LiAlH_4$, suspended in 1000 mL of anhydrous THF, and stirred for 15 min. While the solution was being stirred vigorously and under a N_2 atmosphere a solution of 0.10 mol of methyl aryl ketone in 75 mL of THF to the black suspension was added dropwise from the addition funnel. After complete addition (ca. 10 min) of the substrate, the reaction mixture was refluxed while stirring efficiently for 110 h. The reaction mixture was hydrolyzed carefully with H_2O, tranferred to a separatory funnel, and efficiently extracted with 2 × 500 mL portions of petroleum ether. The combined extracts were dried over anhydrous $MgSO_4$, the solvent was rotoevaporated (ca. 28 °C (25 mm)), and the residue was chromatographed on silica gel (25:1 adsorbant to product), eluting the alkene with CCl_4-$CHCl_3$ (1:1) until appearance of the pinacol (detected by IR). The yield of pure but isomeric cis–trans alkenes was 73% based on aryl methyl ketone.

The separation of this isomer mixture into pure *cis*- and *trans*-2-butenes was achieved by dry column chromatography on silica gel eluting with CCl_4. For maximum efficiency the silica gel was baked out in a muffle furnace at 250 °C for 4 h. A 100-cm long and 20-mm i.d. Nylon hose was charged with 200 g of silica gel per g of the isomer product mixture. The latter was dissolved in a minimum amount of CCl_4, placed on the dry column, and eluted with CCl_4 until appearance of the alkene in the eluant. The nylon column was cut into 3-cm sections and each section was efficiently triturated with CCl_4. The solvent was rotoevaporated (ca. 0 °C (20 mm)) and the residue weighed and examined by ^{1}H NMR.

A separate dry column chromatography run was made for each gram of isomeric product mixture. Corresponding fractions rich in one of the isomers from the individual chromatography runs were combined and rechromatographed as described above. Final purification was achieved by sublimation. In this way ca. 1 g of each isomerically pure substrate was obtained, confirming isomer purity by ^{1}H NMR. The results are summarized in Table I.

General Singlet Oxygenation Procedure. A CCl_4 solution ca. 0.1 M in substrate, 0.1 M in standard, and ca. 0.003 M in tetraphenylporphyrin (TPP) was placed into a 100-mL, two-necked, round-bottomed flask which was equipped with a magnetic spinbar. One of the necks was connected by means of a three-way stopcock to a rubber balloon holding ca. 3 L of pure oxygen gas; the other neck was covered with a rubber septum to permit periodic sample removal. While being stirred magnetically and having the three-way stopcock positioned in such a way that the reaction mixture was under oxygen gas pressure from the balloon, the reaction mixture was irradiated with a General Electric 150 Watt Sodium street lamp. Periodically aliquots were syringed directly into an NMR tube and the progress of the singlet oxygenation monitored by ^{1}H NMR, following substrate and internal standard consumption and/or product formation. The relative areas under the proton resonances were determined by direct electronic integration. Each substrate–internal standard pair was run in triplicate and integrated at least five times. Statistical corrections for the number of protons were made. The relative rates are summarized in Table III.

For structure identification of the substrate hydroperoxide product **2**, the singlet oxygenation was performed in the absence of the internal standard, using substrate concentrations ca. 1 M. After complete consumption of the substrate NMR signal, the solution was titrated for peroxide by iodometry, affording better than 95% purity based on initial substrate concentration. ^{1}H NMR and IR confirm the expected allylic hydroperoxide structure **2** (Table II). Attempts to concentrate and isolate the labile hydroperoxides led to isomerization and decomposition.

Assignment of Photoelectron Spectra. To interprete the measured photoelectron spectra we made use of Koopmans' theorem ($-\epsilon_j = I_{v,j}$).[11] In this assumption the negative value of the orbital energy, ϵ_j, is set equal to the vertical ionization potential, $I_{v,j}$. The orbital energies were derived by a modified HMO procedure.[12]

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Registry No.—Methyl phenyl ketone, 98-86-2; methyl β-naphthyl ketone, 93-08-3; methyl α-naphthyl ketone, 941-98-0.

References and Notes

(1) Paper No. 73 in the Cyclic Peroxide Series.
(2) (a) NIH Career Development Awardee, 1978–80. (b) Summer Research Participant in the Support of Biomedical Education (SUBE) sponsored by the NIH-MBS program. (c) On leave of absence from Suzuka Technological College.
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