methylformamide dimethyl acetal. The column was washed with chloroform. The combined filtrate and washings were evaporated in vacuo to a foam (2.96 g, quantitative yield) which was used directly in the next step.

Reaction of 18 with Guanidine. Guanidine hydrochloride (9.0 g, 94 mmol) was added to ethanolic sodium ethoxide (prepared by dissolving 1.6 g of metallic sodium in 100 mL of ethanol) and the mixture stirred for 5 min. Sodium chloride which precipitated was removed by filtration and the filtrate concentrated in vacuo. A solution of **18** (2.96 g, 5.94 mmol) in ethanol (10 mL) was added to the residue, and the mixture was refluxed for 4 h. After cooling to room temperature, the mixture was poured onto ice–water (600 mL) with stirring. The suspension was neutralized with acetic acid to pH ~6. The precipitate was collected by filtration, washed with water (200 mL), and redissolved in ethanol, and the solution was concentrated to dryness in vacuo. The residue was dissolved in methanol. Silica gel G60 (100 mL) was added to the solution, and the suspension was concentrated to dryness in vacuo. The residue was placed on a silica gel column (34 × 3.5 cm), and the column was washed successively with 200 mL each of chloroform, 1% ethanol in chloroform, 2% ethanol in chloroform, and 4% ethanol in chloroform. 5′-*O*-Trityl-2′-deoxy-*α*-*ψ*-isocytidine (the *α* isomer of **19**) was then eluted from the column with 8% ethanol in chloroform (1.5 L). Evaporation of the eluent afforded a foam (1.17 g, 42%).

Anal. Calcd for $C_{28}H_{27}N_3O_4{\cdot}0.5H_2O$: C, 70.28; H, 5.90; N, 8.78. Found: C, 69.97; H, 5.84; N, 8.53.

5′-*O*-Trityl-2′-deoxy-*ψ*-isocytidine (**19**) was eluted with 16% ethanol in chloroform (1.5 L). Evaporation of the solvent and recrystallization of the semicrystalline residue from ethanol afforded 1.06 g (38%) of **19**, mp 198–201 °C dec.

Anal. Calcd for $C_{28}H_{27}N_3O_4$: C, 71.62; H, 5.80; N, 8.95. Found: C, 71.36; H, 6.00; N, 8.88.

2′-Deoxy-*ψ*-isocytidine (9, R = H) from 19. Compound **19** (375 mg, 0.8 mmol) suspended in 88% formic acid (10 mL) was vigorously stirred for 3 min at room temperature. The mixture was quickly frozen in a dry ice–acetone bath and then lyophilized. The residue was suspended in water (10 mL), insoluble triphenylcarbinol removed by filtration, and the filtrate lyophilized. The residue was crystallized from ethanol to afford 152 mg (84%) of **9** (R = H), mp 165–167 °C. The ^{1}H NMR spectrum of this sample was identical with that of an authentic sample previously obtained by the alternate procedure.

Acknowledgment. We thank Kyowa Hakko Kogyo Co. Ltd., Tokyo, for *ψ*-uridine used in this study.

Registry No. **1**, 1445-07-4; **4**, 39967-60-7; **5**, 69265-05-0; **6**, 65358-15-8; **7**, 65358-16-9; **8**, 78064-58-1; **9** (R = H), 65358-18-1; (R = H) (*α* isomer), 65358-19-2; **9** (R = Ac), 65449-72-1; **10** (R = H), 78064-59-2; **10** (R = Ac), 78064-60-5; **11**, 13860-38-3; **12**, 78064-61-6; **13**, 78064-62-7; **14**, 78064-63-8; **15**, 78064-64-9; **16**, 78109-46-3; **17**, 78064-65-0; **18**, 78064-66-1; **19**, 78064-67-2; **19** (*α* isomer), 78064-68-3; guanidine·HCl, 50-01-1; trityl chloride, 76-83-5; (thiocarbonyl)diimidazole, 6160-65-2.

Photochemistry of Alkenes. 7. *E* ⇄ *Z* Isomerization of Alkenes Sensitized with Benzene and Derivatives

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Contrary to numerous previous reports placing the $(E/Z)_{pss}$ ratios from benzene-sensitized isomerization of various alkenes at unity, the $(E/Z)_{pss}$ ratios for alkenes **1**–**4** (Table I) have been found to (a) differ from unity, with the less highly strained isomer predominating, (b) vary depending on the structure of the alkene, and (c) bear an apparently linear relationship with the triplet excitation energy of the sensitizer. The results are tentatively interpreted in terms of "nonvertical" energy transfer, with transfer occurring more efficiently to the thermodynamically less stable isomer. Possible difficulties with the quantitative aspects of this interpretation are discussed. Of several sensitizers evaluated for efficiency in effecting *E* ⇄ *Z* isomerization of 3,4-dimethyl-2-pentene (**2**) (Table III), *p*-xylene and phenol were found to be superior. The latter has the added advantage of being easily separated from the alkene by extraction with base.

It is generally accepted that the lowest lying triplet excited state of ethene and its simple alkyl derivatives is π,π^*.[1] Except for highly constrained cycloalkenes, the principal chemical property of this state is to undergo rotation about the double bond, with the resulting formation of a mixture of the *E* and *Z* isomers of the alkene.[2] Previous reports have indicated that high-energy triplet sensitizers, such as benzene, afford *E*/*Z* photostationary state ratios [$(E/Z)_{pss}$] of unity.[3,4] Such a result was reasonable in light of the then-accepted value of ≤82 kcal/mol for the vertical triplet excitation energy (E_T) of alkenes but is questionable in view of recent reports placing the value considerably higher.[5] We report here that benzene and its simple derivatives in fact afford $(E/Z)_{pss}$ ratios which (a) differ from unity, with the less highly strained isomer predominating, (b) vary depending on the structure of the alkene, and (c) bear an apparently linear relationship with the triplet excitation energy (E_T) of the sensitizer.

Results

The data obtained from *E*/*Z* isomerization of alkenes

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[1] For a review of the excited states of alkenes see A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

[2] For a review of the photobehavior of alkenes in solution see P. J. Kropp, *Org. Photochem.*, **4**, 1 (1979).

[3] (a) 2-Pentene, 2-hexene, 2-heptene, and 2-octene (1.0): M. A. Golub, C. L. Stephens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966), and M. A. Golub and C. L. Stephens, *J. Phys. Chem.*, **70**, 3576 (1966); (b) 2-butene (1.0 ± 0.1) and 2-pentene (0.9 ± 0.1): M. Tanaka, M. Kato, and S. Sato, *Bull. Chem. Soc. Jpn.*, **39**, 1423 (1966), and S. Sato *Pure Appl. Chem.*, **16**, 87 (1968); (c) 2-butene (0.92): E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968); (d) 2-octene (unity): R. R. Hentz and R. M. Thibault, *J. Phys. Chem.*, **77**, 1105 (1973); and (e) 2-butene (1.1): G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967).

[4] By contrast low-energy sensitizers, usually carbonyl compounds, afford $(E/Z)_{pss}$ ratios approaching thermodynamic values because of competing isomerization via a Schenck-type mechanism; see N. C. Yang, J. I. Cohen, and A. Shani, *J. Am. Chem. Soc.*, **90**, 3264 (1968), and J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969).

[5] (a) R. S. Mulliken, *J. Chem. Phys.*, **66**, 2448 (1977); (b) W. M. Flicker, O. A. Mosher, and A. Kuppermann, *Chem. Phys. Lett.*, **36**, 56 (1975); W. M. Flicker, O. A. Mosher, and A. Kuppermann, private communication; and (c) I. Sauers, L. A. Grezzo, S. W. Staley, and J. H. Moore, Jr., *J. Am. Chem. Soc.*, **98**, 4218 (1976).

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Table I. E/Z Isomerization of Alkenes 1-5 Sensitized with Benzene and Derivatives[a]

sensitizer	E_T, kcal/mol[b]	solvent	$(E/Z)_{pss}$[c] 1	2	3	4[d]	5[e]
benzene[f]	84.3		1.07 1.08[g]	1.57		18	0.05
toluene	82.5	ether	1.26	1.61		22	0.05
o-xylene	82.1	ether			1.13		
phenol	81.7	ether			1.12		
p-xylene	80.4	ether	1.41	1.92	1.19		0.05
		pentane		1.96			
		methanol	1.61	1.79			
mesitylene	80.3	ether	1.38	1.88			0.04
durene	80.0	ether	1.43	1.98			
pentamethylbenzene		ether		*h*			
hexamethylbenzene	78.4	ether	*i*	*i*			

[a] Irradiations were conducted at 254 nm, using 20-mL solutions 0.2 M in sensitizer and 0.1 M in alkene and contained in a quartz tube suspended in a RPR-100 Rayonet Photochemical Reactor. [b] Reference 7. [c] Average of two runs, one starting with each isomer; values agreed within ±4%. [d] Determined starting with the E isomer only. [e] Reference 6. [f] Irradiations were run using 20-mL benzene solutions which were 0.1 M in alkene. [g] Solution was 0.05 M in alkene. [h] Photostationary state had not been reached after extended irradiation. [i] No detectable isomerization.

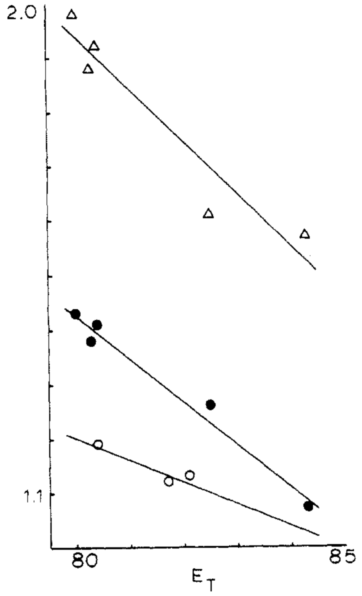


Figure 1. Plot of $(E/Z)_{pss}$ vs. sensitizer E_T for alkenes 1 (●), 2 (△), and 3 (○).

Table II. Thermodynamic Equilibration of Alkenes 1-4[a]

	1	2	3	4
$(E/Z)_{equil}$[b]	3.30	3.46	10.55	>500
ΔG_{equil}, kcal/mol	−0.73	−0.75	−1.43	<−3.8

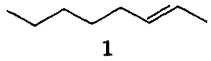
[a] Determined at 306 K, using 25-mL solutions which were 48 mM in diphenyl sulfide and 23.5 mM in alkene, contained in a quartz tube suspended in a merry-go-round apparatus located in a thermostatically controlled water bath, and irradiated with a 450-W medium-pressure mercury lamp. Isomer ratios were determined gas chromatographically relative to an internal hydrocarbon standard. [b] Average of two runs, one starting with each isomer.

Table III. Comparative $E \rightleftarrows Z$ Isomerization of 3,4-Dimethyl-2-pentene (2)[a]

sensitizer	isomerization, %
phenol	22
p-xylene	24
mesitylene	14
durene	16

[a] Irradiations were conducted simultaneously at 254 nm, using 10-mL solutions which were 0.2 M in sensitizer and 0.1 M in alkene 2 and were contained in a Vycor tube placed in a merry-go-round apparatus suspended in a RPR-100 Rayonet Photochemical Reactor. The solutions were deaerated by six freeze-pump-thaw cycles prior to irradiation.

1-4 are summarized in Table I, along with those previously reported for cyclooctene (5).[6] The $(E/Z)_{pss}$ ratios vary as a function of both the alkene and the E_T of the sensitizer. Moreover, as seen in Figure 1, the ratios for alkenes 1-3 vary linearly with the E_T of the sensitizer over the range studied (correlation coefficients of −0.94 to −0.99). Alkenes 4 and 5, which are highly strained in their Z or E configuration, respectively, afforded ratios which differ greatly from those of alkenes 1-3. Although in each case the thermodynamically more stable isomer predominates at the photostationary state, the $(E/Z)_{pss}$ ratios are significantly different from the thermodynamic ratios determined by irradiation of diphenyl sulfide in the presence of each isomer (Table II).[8]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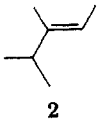
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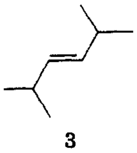
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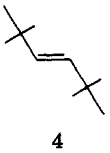
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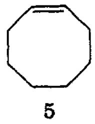
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Irradiations using benzene as the sensitizer had to be run neat in order to avoid substantial yellowing of the solution due to competing reactions by singlet excited sensitizer.[9] Benzene—and, to a lesser extent, toluene—required extended irradiation times because of the formation of side products which made the solution opaque. The other sensitizers were free of this difficulty. Mesitylene and *o*-xylene irradiations were complicated by isomerization of the sensitizer to 1,2,4-trimethylbenzene or *p*-xylene, respectively.[10] Pentamethylbenzene was highly inefficient and the hexamethyl derivative was ineffective as a sensitizer. As seen in Table III, a study of the relative efficiencies of several sensitizers for effecting the $E \rightleftarrows Z$ isomerization of 2 revealed a comparably high effectiveness of either *p*-xylene or phenol.

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(6) Y. Inoue, S. Takamuku, and H. Sakurai, *J. Phys. Chem.*, 81, 7 (1977).

(7) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973, pp 34-35.

(8) For a discussion of this general procedure for determining thermodynamic ratios, see C. Moussebois and J. Dale, *J. Chem. Soc. C*, 260 (1966).

(9) High benzene concentrations result in the formation of a benzene singlet excimer which decays more efficiently to triplet benzene, thereby reducing the concentration of monomeric singlet benzene and increasing the yield of triplet benzene (cf. ref 3d and references cited therein): $^1B^* + B \rightarrow [BB]^* \rightarrow {}^3B^* + B$.

(10) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **86**, 2307 (1964); L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, 87, 675 (1965).

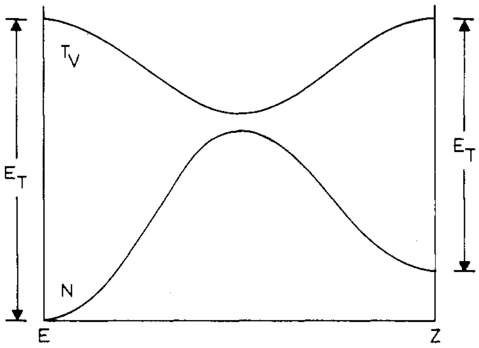

Figure 2. Ground-state (N) and $^3(\pi,\pi^*)$ excited-state (T_V) potential energies as a function of twisting about the double bond.

Discussion

The sensitized $E \rightleftarrows Z$ isomerization of alkenes is generally thought to involve generation of either the E or Z $^3(\pi,\pi^*)$ state, depending on the configuration of the ground-state molecule, followed by decay of each of these intermediates to a common orthogonal species by loss of vibrational energy and twisting about the carbon–carbon bond (Figure 2). Subsequent intersystem crossing to the ground state is facilitated by the close approach of the excited- and ground-state potential-energy surfaces. The resulting orthogonal species lies at an energy maximum and rapidly decays by twisting about the σ bond to afford either the E or Z ground-state isomer. The $(E/Z)_{\mathrm{pss}}$ ratio is thus a function of both the ratio for excitation of the E and Z isomers and the ratio for decay of the orthogonal intermediate to the E or Z isomer. If, as is generally assumed, decay from the orthogonal species occurs with equal probability to the E and Z ground-state isomers, the $(E/Z)_{\mathrm{pss}}$ ratio should show an inverse dependence on the E/Z excitation ratio. When it was earlier believed that for alkenes $E_T \leq 82$ kcal/mol, it was apparently assumed that energy transfer to either isomer from benzene would be exothermic and, hence, that the excitation ratio would also be unity. Thus an $(E/Z)_{\mathrm{pss}}$ ratio of unity was expected, as seemed to be observed experimentally.[3]

However, a recent analysis of the oxygen-perturbed spectrum of ethene has placed E_T at 99 kcal/mol.[5a] This has been corroborated by low-energy variable-angle electron-impact spectroscopy, which has placed E_T at 94.5–99.6 kcal/mol for a variety of alkenes,[5b] and by helium ion impact energy-loss spectroscopy, which has afforded values of 95.9–99.2 for a series of (Z)-cycloalkenes and 88.8 for the highly strained (E)-cyclooctene.[5c] These results suggest that transfer of triplet energy from the presently discussed sensitizers to both the E and Z isomers of most simple alkenes is endothermic and "nonvertical".[11-14] Since E_T is reported to be somewhat lower for the more strained isomer of an E/Z pair,[5b,c] energy transfer should occur more efficiently to that isomer, resulting in a pumping effect which affords an $(E/Z)_{\mathrm{pss}}$ ratio favoring the less highly strained isomer, as observed. Indeed, the present results can be regarded as support for the contention that $E_T \gg 82$ kcal/mol. The proposed occurrence of triplet energy transfer via a "nonvertical" path is also consistent with the low quantum yields reported for benzene-sensitized isomerization of (E)-2-octene (~0.05–0.1).[3d]

Although the present results are qualitatively explained by the above argument, comparison of the $(E/Z)_{\mathrm{pss}}$ data of Table II with the thermodynamic equilibration data of Table III reveals some apparent inconsistencies. Thus although the difference in free energy between the E and Z isomers ($\Delta G_{\mathrm{equil}}$) is almost identical for **1** and **2**, they afford significantly different $(E/Z)_{\mathrm{pss}}$ ratios. For **3** and **4** $\Delta G_{\mathrm{equil}}$ is substantially more negative, yet **3** affords $(E/Z)_{\mathrm{pss}}$ ratios significantly less than for **1** and **2**, whereas **4** affords substantially greater $(E/Z)_{\mathrm{pss}}$ ratios. These discrepancies may indicate that the decay ratio is not always unity for alkenes. Alternatively, there may be a steric effect on the energy-transfer process or ΔE_T may not follow $\Delta G_{\mathrm{equil}}$.[15] Finally, it is not clear from the available data whether the ineffectiveness of pentamethyl- and hexamethylbenzene as sensitizers for the $E \rightleftarrows Z$ isomerization of olefins is due to the E_T being below a critical value, a steric effect on the energy-transfer process, or inefficiency in generating the triplet excited state of the sensitizer.

Experimental Section

Materials. Alkenes were obtained from Chemical Samples except for (Z)-**3** and (E)-**4**, which were purchased from Pfaltz and Bauer and Tridon-Fluka, respectively, and were used without further purification. Sensitizers were used as purchased from the following sources: benzene (Certified ACS) from Fisher, toluene (Spectrophotometry grade) and p-xylene (Chromatoquality grade) from MCB, o-xylene and mesitylene (Organic Reagent) from Mallinckrodt, durene and hexamethylbenzene from Eastman, pentamethylbenzene (99%) from Aldrich, and phenol (Reagent grade) from Baker and Adamson. Diphenyl sulfide (Gold Label) was obtained from Aldrich. Methanol was distilled from calcium hydride. Alkene-free pentane was obtained by allowing a solution of 5 mL of bromine in 3 L of pentane (Phillips Pure grade) to stand overnight, followed by quenching of excess bromine with a basic solution of sodium thiosulfate, drying over anhydrous sodium sulfate, and carefully fractionating through an 18-in. × 1-in. column packed with glass beads.

Analyses. E/Z ratios were determined by gas chromatography relative to a hydrocarbon internal standard and corrected for measured response factors.

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Registry No. (E)-**1**, 13389-42-9; (Z)-**1**, 7642-04-8; (E)-**2**, 4914-92-5; (Z)-**2**, 4914-91-4; (E)-**3**, 692-70-6; (Z)-**3**, 10557-44-5; (E)-**4**, 692-48-8; (Z)-**4**, 692-47-7.

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(11) Although these are gas-phase values, there is little reason to believe that E_T's are substantially lower in solution.

(12) For a recent discussion of "nonvertical" triplet energy transfer, see V. Balzani, F. Bolletta, and F. Scandola, *J. Am. Chem. Soc.*, 102, 2152 (1980), and references cited therein.

(13) It is assumed that the observed $E \rightleftarrows Z$ isomerization is due principally to triplet, rather than singlet, energy transfer since the rate constants for triplet and singlet quenching of benzene by (E)-2-octene (1) are 3.4×10^9 and 5.4×10^7 M^{-1} s^{-1}, respectively; see ref 3d.

(14) Since mass balances generally exceeded 90%, $(E/Z)_{\mathrm{pss}}$ ratios were not substantially influenced by unequal rates of addition of the E and Z isomers of the alkene to singlet excited sensitizer.

(15) For a prior example of steric hindrance to energy transfer, involving substituted benzophenones and stilbene, see W. G. Herkstroeter, L. B. Jones, and G. S. Hammond, *J. Am. Chem. Soc.*, 88, 4777 (1966).