Organic Photochemistry. VI. *cis–trans* Photoisomerization of 1-Phenyl-2-butene by Intramolecular Energy Transfer[1,2]

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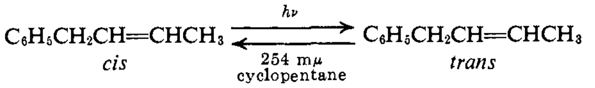
Abstract: The solution-phase, intramolecular, photosensitized *cis–trans* isomerization of 1-phenyl-2-butene has been studied. The photostationary state at 25° is 1.19 and the quantum yields (1.96×10^{-2} *M;* 254 mμ) are $\phi_{t \to c} = 0.20$ and $\phi_{c \to t} = 0.16$. The isomerization can be quenched by *trans*-2-hexene and *cis*-piperylene but not by oxygen. Quenching by the hexene is not diffusion controlled, being about 100 times less efficient than that observed for piperylene. The rate of intramolecular energy transfer is calculated as 2.0×10^8 sec^{-1}. The quantum yield for intersystem crossing of the phenyl group is estimated to be at least 0.36.

We recently reported[3] that *cis–trans* photoisomerization of 1-phenyl-2-butene can be achieved through irradiation of this compound with light absorbed by the aromatic ring; the reaction is considered to be an example of intramolecular photosensitization.



$$\underset{cis}{C_6H_5CH_2CH{=}CHCH_3} \underset{\substack{254\ m\mu \\ \text{cyclopentane}}}{\overset{h\nu}{\rightleftarrows}} \underset{trans}{C_6H_5CH_2CH{=}CHCH_3}$$

Further work in our laboratories has since uncovered other photochemical reactions using nonconjugated donor–acceptor pairs, *e.g.*, ketone–olefin, phenyl–ester, and phenyl–ketone.[2–4] In addition to being intrinsically interesting, these systems are potentially useful as synthetic tools (for induction of a reaction at one of several *apparently* identical chromophores) and as probes into the geometrical requirements of triplet-energy transfer. The aryl–olefin system is the most promising for the latter purpose because the reaction is clean and easily followed. However, before more complicated molecules can be fruitfully studied, the simplest analog (*e.g.*, phenylbutene) must be examined in detail so as to provide data on the rate, quantum efficiency, and per cent of intramolecular energy transfer. Knowledge of the degree to which the phenyl group undergoes intersystem crossing in the solution phase is also required.

The intermolecular analog of this reaction (*i.e.*, benzene-sensitized isomerization of olefins) has been reported for both the liquid[3,5–8] and gas[9–13] phases and shown[6,9,10] to proceed *via* triplet-energy transfer. The phenomenon of intramolecular triplet-energy transfer is now well documented, having been detected through observation of chemical reaction at the acceptor chromophore[3,14–17] as well as by emission spectroscopy.[18–20]

Results

A. Preparative Experiments. Irradiation of a solution (pentane, hexane, cyclopentane, ether) of *trans*-1-phenyl-2-butene (*ca.* 1×10^{-2} *M*) using either filtered light (248–282 mμ) or light from a Vycor-enclosed, low-pressure mercury lamp (254 mμ) gave rapid conversion to a single new substance. The product was isolated by vpc and identified as the isomeric *cis*-1-phenyl-2-butene (*cf.* Experimental Section for spectral and analytical data). More recent large-scale experiments have involved irradiation of 3 g of phenylbutene in 100 ml of solvent using the low-pressure lamp. A 1:1 ratio of isomers is produced in 30 hr. All the quantitative data described below were obtained using cyclopentane as solvent at a temperature of 25.0 ± 0.1°.

B. Photostationary State. The photostationary-state ratio of the 1-phenyl-2-butene isomers was determined using the low-pressure lamp with the results shown in Table I. The observed ratio of $(cis)_s/(trans)_s = 1.19 \pm 0.02$.

Table I. Photostationary State of 1-Phenyl-2-butene (25.0 ± 0.1°)

Original isomer	$(cis)_s/(trans)_s$
trans	1.16
	1.19
	1.18
	1.18
cis	1.21
	1.20
Av	1.19 ± 0.02

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[1] Part V: H. Morrison in "The Chemistry of the Nitro and Nitroso Groups," H. Feuer, Ed., John Wiley and Sons, Inc., New York, N. Y., in press.

[2] Presented, in part, at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, abstract P-137.

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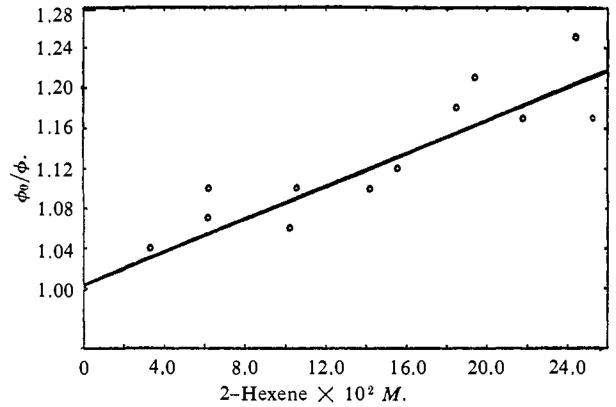

Figure 1. Stern-Volmer plot for the quenching of *trans*-1-phenyl-2-butene isomerization by *trans*-2-hexene (cyclopentane solution, 25.0 ± 0.1°).

C. Quantum Yield Measurements. The quantum yields for interconversion of the *cis* and *trans* isomers were obtained with the low-pressure lamp and the use of uranyl oxalate actinometry. The data are shown in Table II. From these data, the quantum yield for conversion of the *trans* to *cis* isomer may be taken as $\phi_{t \rightarrow c} = 0.20$; the analogous number for conversion of *cis* to *trans* is $\phi_{c \rightarrow t} = 0.16$.

Table II. Quantum Yields for Isomerization of 1-Phenyl-2-butene (25.0 ± 0.1°)

Isomerization	λ_{irrad}, mμ		Quantum yield
trans to *cis*	254		0.20
			0.19
			0.19
			0.19
			0.21
			0.20
		Av	0.20 ± 0.01
cis to *trans*	254		0.15
			0.16
			0.15
			0.16
		Av	0.16 ± 0.01

D. Quenching Experiments. (i) *trans*-2-Hexene. Cyclopentane solutions of *trans*-1-phenyl-2-butene (3.51×10^{-3} *M*) and *trans*-2-hexene (3.31–24.4×10^{-2} *M*) were irradiated on a turntable using the low-pressure lamp (25.0 ± 0.1°). The data are shown in Figure 1 as a Stern-Volmer plot of ϕ_0/ϕ *vs.* quencher concentration. The slope, as determined by the method of least squares, is 0.83 ± 0.08 l. mol^{-1}; the calculated intercept is 1.01.

(ii) *cis*-Piperylene. These quenching data were obtained in the same fashion as were those described above, but because of the greater efficiency of piperylene as a quencher for this reaction, the diene concentrations were varied from 2.13×10^{-3} *M* to 17.9×10^{-3} *M*. The data were corrected for absorption of light by the quencher and the solutions checked by vpc to confirm that the total phenylbutene concentration had not changed during photolysis (see Experimental Section). The Stern-Volmer plot is shown in Figure 2; the calculated slope is 79.6 ± 3.7 l. mol^{-1} and the intercept is 0.994.

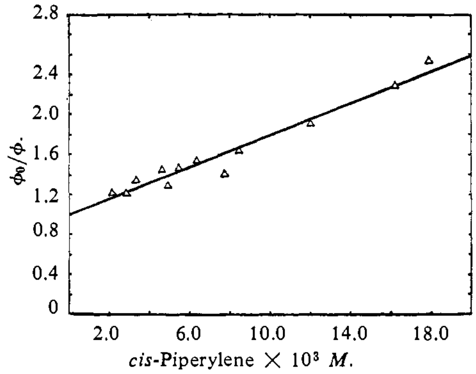

Figure 2. Stern-Volmer plot for the quenching of *trans*-1-phenyl-2-butene isomerization by *cis*-piperylene (cyclopentane solution, 25.0 ± 0.1°).

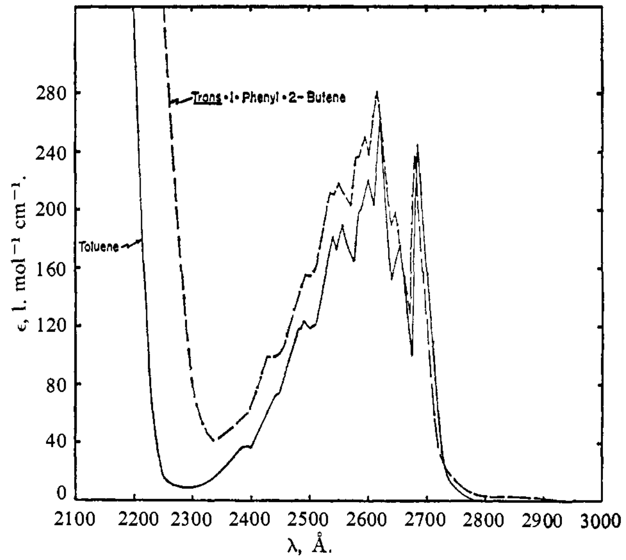

Figure 3. Ultraviolet absorption spectra of *trans*-1-phenyl-2-butene and toluene (determined in cyclopentane solution).

(iii) Oxygen. In two turntable experiments, a solution of *trans*-phenylbutene saturated with oxygen was included among those degassed with argon. The quantum yields for isomerization of these samples were 0.18 and 0.19.

E. Absorption Spectra. The absorption spectra of *trans*-1-phenyl-2-butene and toluene are displayed in Figure 3. The extinction coefficient for the *trans* isomer at 254 mμ is 212; the analogous value for the *cis* isomer is 217.

Discussion

A. Proposed Mechanism for the Photoisomerization. The mechanism which we suggest for the light-induced isomerization of 1-phenyl-2-butene is given below. The donor and acceptor chromophores are treated as separate entities although the uv absorption spectrum indicates small but finite interaction between the two groups (Figure 3). A triplet donor is invoked in the energy transfer steps (4–6), an assumption amply supported by the literature[6,8–10] as well as by our own quenching experiments with dilute solutions of piperylene. We feel the transfer is predominantly intramolecular (eq 4) at the concentrations of phenylbutene studied (*ca.* 3×10^{-3} *M*) because the addition of an equimolar amount of *trans*-2-hexene leads to little observable isomerization of the aliphatic olefin. In a more quantitative sense, the relative rates for the intra- *vs.* intermolecular processes can be derived from quenching experiments and are discussed below. The rate constants k_{ic}, k_d, k_q, and k_r are assumed to be independent of olefin stereochemistry. Although olefin excitation leads initially to the Franck–Condon *cis* and *trans* triplet states, we have assumed rapid decay to a twisted (*e.g.*, perpendicular) triplet (P-^{3}X) and the mechanism has been simplified accordingly

$$\text{P-}t \xrightarrow[254\ \text{m}\mu]{h\nu} {}^1\text{P-}t \qquad \text{P-}c \xrightarrow[254\ \text{m}\mu]{h\nu} {}^1\text{P-}c \tag{1}$$

$${}^1\text{P-}t \xrightarrow{k_{ic}} {}^3\text{P-}t \qquad {}^1\text{P-}c \xrightarrow{k_{ic}} {}^3\text{P-}c \tag{2}$$

$${}^3\text{P-}t \xrightarrow{k_d} \text{P-}t \qquad {}^3\text{P-}c \xrightarrow{k_d} \text{P-}c \tag{3}$$

$${}^3\text{P-}t \xrightarrow{k_1} \text{P-}^3\text{X} \qquad {}^3\text{P-}c \xrightarrow{k_2} \text{P-}^3\text{X} \tag{4}$$

$${}^3\text{P-}t \text{ (or } {}^3\text{P-}c) + \text{P-}c \text{ (or P-}t) \xrightarrow{k_r} \text{P-}^3\text{X} + \text{P-}t \text{ (or P-}c) \tag{5}$$

$${}^3\text{P-}t + \text{Q} \xrightarrow{k_q} \text{P-}t \qquad {}^3\text{P-}c + \text{Q} \xrightarrow{k_q} \text{P-}c \tag{6}$$

$$\text{P-}^3\text{X} \xrightarrow{k_t} \text{P-}t \qquad \text{P-}^3\text{X} \xrightarrow{k_c} \text{P-}c \tag{7}$$

where P-*t* and P-*c* refer to *trans*- and *cis*-1-phenyl-2-butene, respectively, and the superscripts 1 and 3 indicate singlet and triplet excited states of the phenyl moiety.

This mechanism leads to the following expression for the photostationary state

$$\frac{(\text{P-}c)_s}{(\text{P-}t)_s} = \frac{\epsilon_t \phi_{\text{et}(t)} k_c}{\epsilon_c \phi_{\text{et}(c)} k_t} \tag{8}$$

where ϵ_t and ϵ_c represent the extinction coefficients at 254 mμ for the *trans* and *cis* isomers and $\phi_{\text{et}(t)}$ and $\phi_{\text{et}(c)}$ represent the fraction of phenyl triplets which transfer energy to the olefin in the *trans* and *cis* isomers, respectively. Equation 9 is obtained by insertion of the observed values for ϵ_t and ϵ_c.

$$\frac{(\text{P-}c)_s}{(\text{P-}t)_s} = 0.98\frac{\phi_{\text{et}(t)} k_c}{\phi_{\text{et}(c)} k_t} \tag{9}$$

The equations for the quantum yields of *trans–cis* and *cis–trans* isomerization are shown in (10) and (11)

$$\phi_{t\rightarrow c} = \phi_{\text{ic}}\phi_{\text{et}(t)}\frac{k_c}{k_t + k_c} \tag{10}$$

$$\phi_{c\rightarrow t} = \phi_{\text{ic}}\phi_{\text{et}(c)}\frac{k_t}{k_t + k_c} \tag{11}$$

where ϕ_{ic} is the fraction of phenyl excited singlet states which undergo intersystem crossing to triplets. Dividing eq 10 by eq 11 leads to an expression (12) relating the two quantum yields for isomerization. *A comparison of*

$$\frac{\phi_{t\rightarrow c}}{\phi_{c\rightarrow t}} = \frac{\phi_{\text{et}(t)} k_c}{\phi_{\text{et}(c)} k_t} \tag{12}$$

eq 9 and 12 establishes the requirement that the ratio of the quantum yields for isomerization should be equal to 1.02 times the photostationary state. Reference to Tables I and II will show that this is, in fact, the case, *e.g.*

$$\frac{(\text{P-}c)_s}{(\text{P-}t)_s} = \frac{\epsilon_t \phi_{t\rightarrow c}}{\epsilon_c \phi_{c\rightarrow t}} = 1.2 \tag{13}$$

B. Solution-Phase Intersystem Crossing of the Phenyl Group. Equation 14 is derived from the addition of eq 10 and 11 and the assumption[21] that $\phi_{\text{et}(t)} = \phi_{\text{et}(c)} = \phi_{\text{et}}$. A knowledge of one of these is thus sufficient for the assignment of a value to the other. Considering the

$$\phi_{t\rightarrow c} + \phi_{c\rightarrow t} = \phi_{\text{ic}}\phi_{\text{et}} = 0.36 \pm 0.02 \tag{14}$$

distance between the two functional groups in the phenylbutene molecule and the rapid rate of energy transfer observed (see below), the assumption of a value for $\phi_{\text{et}} = 1$ would seem reasonable, and substitution of this number into eq 14 results in ϕ_{ic} equal to 0.36 ± 0.02.[22] By contrast, the literature contains ϕ_{ic}'s of 0.24 for benzene in solution[23] (not possible in this case because ϕ_{et} would be greater than one), 0.48 for toluene in an EPA glass at 77°K (our calculation from the reported[24] ratio of phosphorescence to fluorescence), and 0.63 to 0.71 for benzene in the gas phase.[10,25,26]

An additional value of ϕ_{ic} for benzene in solution may be extracted from data available for the benzene-sensitized isomerization of stilbene. Krongauz[5] measured the quantum yield for this *trans–cis* isomerization and recognized the validity of an eq 15 analogous to our eq 10

$$\phi_{t\rightarrow c} = \phi_{\text{ic}}\frac{k'_c}{k'_t + k'_c} = 0.25 \tag{15}$$

where k' refers to the stilbene system and ϕ_{et} has been assumed equal to one. What was not recognized was that the necessary ratio of rate constants was already available from photostationary-state data for the "high-energy" sensitized stilbene isomerization.[27] In eq 16 and 17, this ratio is calculated to be 0.6 and the resultant ϕ_{ic} is 0.42.

$$(cis)_s/(trans)_s = k'_c/k'_t = 1.5 \tag{16}$$

$$\frac{k'_c}{k'_t + k'_c} = \frac{1.5}{1.5 + 1} = 0.6 \tag{17}$$

C. Quenching of Phenylbutene Isomerization and the Rate Constant of Intramolecular Energy Transfer. The quenching experiments described above were carried out with two goals in mind. First, we wanted to confirm the intramolecular character of the energy transfer act and this was accomplished through the data plotted in Figure 1. If the transfer were to any large extent intermolecular, one would expect appreciable quenching by comparable amounts of added 2-hexene; in fact, a tenfold excess of the olefin causes negligible diminution (4%) of the quantum yield for phenylbutene isomerization.

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[21] This assumption is presently being tested. The rapid rate of internal energy transfer in the phenylbutenes should be reflected in a considerable quenching of the phenyl phosphorescence with respect to phenylbutane with comparable emission observed for each of the phenylbutane *cis–trans* isomers. These experiments are presently in progress.

[22] Note that this value for ϕ_{ic} would increase were it to develop that ϕ_{et} was less than one.

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The second objective of these experiments was to obtain data which would enable us to calculate a rate constant (k_1) for the energy-transfer step (*e.g.*, eq 4). Using the mechanism outlined in eq 1–13, and imposing the steady-state condition on ^{3}P-*t* and P-^{3}X, we find that for the *trans–cis* reaction at small conversions

$$\frac{1}{\phi_{t\rightarrow c}} = \frac{k_c + k_t}{k_c}\frac{k_\mathrm{d} + k_1 + k_\mathrm{r}(\mathrm{P}\text{-}t) + k_\mathrm{q}(\mathrm{Q})}{\phi_\mathrm{ic}[k_1 + k_\mathrm{r}(\mathrm{P}\text{-}t)]} \qquad (18)$$

Equation 18 is simplified by the Stern–Volmer treatment ($\phi_0 = \phi$ at (Q) = 0) to give

$$\frac{\phi_0}{\phi} = \frac{k_\mathrm{d} + k_1 + k_\mathrm{r}(\mathrm{P}\text{-}t) + k_\mathrm{q}(\mathrm{Q})}{k_\mathrm{d} + k_1 + k_\mathrm{r}(\mathrm{P}\text{-}t)} \qquad (19)$$

or

$$\frac{\phi_0}{\phi} = 1 + \frac{k_\mathrm{q}(Q)}{k_\mathrm{d} + k_1 + k_\mathrm{r}(\mathrm{P}\text{-}t)} \qquad (20)$$

ϕ_0/ϕ should show a straight-line dependence on (Q) with an intercept equal to one and a slope of $k_\mathrm{q}/[k_\mathrm{d} + k_1 + k_\mathrm{r}(\mathrm{P}\text{-}t)]$. The slope calculated by the least-squares method for the *cis*-piperylene data is equal to 79.6 ± 3.7 l. mol^{-1} and the intercept equal to 0.994. Solution of eq 21 should therefore allow for a deter-

$$\frac{k_\mathrm{q}}{k_\mathrm{d} + k_1 + k_\mathrm{r}(\mathrm{P}\text{-}t)} = 80 \qquad (21)$$

mination of k_1. Since the triplet energy of *cis*-piperylene is 57 kcal/mol[28] and the triplet energy of the phenyl group is *ca.* 84 kcal/mol,[29] the rate of quenching should be diffusion controlled with k_q equal to a calculated[30] value of 1.59×10^{10} l. mol^{-1} sec^{-1}. The upper limit for the k_d of benzene in solution has been estimated[31–33] as 10^6–10^7 sec^{-1} and the upper limit for $k_\mathrm{r}(\mathrm{P}\text{-}t)$ may likewise be placed at 10^6–10^7 sec^{-1} [(P-*t*) = 3.5×10^{-3} *M* and k_r is less than 10^{10} l. mol^{-1} sec^{-1}; *cf.* discussion of the hexene data below]. *Substitution of these numbers into eq 21 leads to a value of* k_1 *equal to* 2.0×10^8 *sec*$^{-1}$.[34]

We were at first somewhat surprised that the slope for the 2-hexene data (Figure 1) is almost 100 times smaller than that observed for *cis*-piperylene.[35] Estimates of the triplet energy of aliphatic olefins have varied from 70 to 80 kcal/mol,[8,36,37] values which should be sufficiently lower than the benzene triplet so as to result in diffusion-controlled energy transfer. *In fact,* k_q *for hexene quenching, when calculated in a like manner to that shown above and using* k_1 *as* 2.0×10^8 *sec*$^{-1}$*, is found to equal* 1.7×10^8 *l. mol*$^{-1}$ *sec*$^{-1}$. The anomaly can be resolved by a recent report on the acetone-photosensitized isomerization of pentene.[38] In this paper, a triplet energy for the olefin of 83 kcal/mol is proposed, to account for the slow ($k_\mathrm{q} = 2 \times 10^7$ l. mol^{-1} sec^{-1}), endothermic (*ca.* 1000 cm^{-1}) transfer observed from acetone (E_t = *ca.* 80 kcal/mol[39]). Energy transfer from benzene to an olefin would thus be exothermic by only 1 kcal and would be expected to be less than diffusion controlled.

The rate constant (k_r) for intermolecular energy transfer from a phenylbutene triplet to the olefin of a second phenylbutene can be assumed to be equal to k_q for hexene, *e.g.*, 1.7×10^8 l. mol^{-1} sec^{-1}. This being the case, *the photoisomerization being observed at the concentrations studied here* (3.5×10^{-3} *M*) *is proceeding about 340 times faster by intra- than by intermolecular transfer.* The rapidity of this internal transfer is reflected in our observation that oxygen produces a negligible depression of the quantum yield. The concentration of a saturated solution of oxygen in cyclopentane can be estimated[40,41] at 2×10^{-2} *M* and oxygen has recently been shown[13] to be only three-tenths as efficient as an olefin (2-butene) in quenching the benzene triplet. These data allow for the calculation of a pseudo-first-order rate constant for oxygen quenching (1×10^6) which is *ca.* 200 times slower than internal energy transfer. Note that our data, when combined with those of Haninger and Lee,[13] require that *oxygen quenching of the benzene triplet is about 100 times less than diffusion controlled.* Finally, the greater magnitude of k_1, by comparison with k_d and k_r, supports our original suggestion that ϕ_et for phenylbutene is close to unity.[21]

Experimental Section

General. Analyses for *cis*- and *trans*-1-phenyl-2-butene were carried out by glpc by using either (1) a 20 ft × 0.25 in. 4% AgBF$_4$–16% Carbowax 20M column in an Aerograph A-90-P chromatograph with attached Sargent recorder and Disc Integrator, or (2) a 20 ft × $^3/_{16}$ in. column of identical composition to that above in a Lab-line ChromAlyzer-100 with an accompanying Leeds and Northrup recorder with Disc Integrator. Preparative separations of *cis*- and *trans*-1-phenyl-2-butene were carried out by using a 10 ft × $^3/_8$ in. 10% AgBF$_4$–20% Carbowax 20M column. *cis*-Decalin was employed as an internal standard and calibration curves of *cis*-decalin with *cis*- and *trans*-1-phenyl-2-butene were constructed. From the slope of the calibration curves and the known weight of added *cis*-decalin, the amount of *cis*- and/or *trans*-1-phenyl-2-butene in any given sample could be determined. Uv spectra were determined on a Cary Model 14 spectrophotometer.

***cis*-1-Phenyl-2-butene.** Typically, 3–4 g (0.023–0.03 mol) of *trans*-1-phenyl-2-butene (Aldrich) was dissolved in about 120 ml of spectral grade hexane contained in a cylindrical Pyrex vessel. Into this vessel was placed a quartz immersion well containing a Hanovia low-pressure, mercury resonance lamp. Argon was slowly bubbled through the solution from the bottom of the photolysis vessel and the solution irradiated for approximately 24 hr. After irradiation, the solvent was removed and the residue distilled. The 1-phenyl-2-butene obtained consisted of a 50:50 mixture of the *cis* and *trans* isomers. The two isomers were separated by preparative glpc; nmr: δ 1.70 (3), 3.32 (2), 5.48 (2), 7.03 (3) (area) (*trans*-1-phenyl-2-butene shows δ 1.65, 3.24, 5.44 and 7.06). The infrared spectrum is similar to that of the *trans* isomer but lacks the 10.4-μ band as-

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(34) The rate of intramolecular energy transfer has been estimated for one other case. The rate for triplet transfer from the ligand to the ion in rare earth chelates has been assigned as 10^{10} sec^{-1}. See ref 18.

(35) Singlet energy transfer to piperylene cannot be rigorously excluded at this time but is considered unlikely at the quencher concentrations used. Emission studies on phenylbutene in the presence of piperylene are in progress, and should singlet quenching appear to be a factor under these conditions, our rate for k_et would have to be revised upwards.

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sociated with a *trans*-disubstituted double bond. The mass spectra of the isomers are identical with parent peaks at *m/e* 132.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.39; H, 8.96.

Photostationary State. Purified 1-phenyl-2-butene (50 to 150 mg, 3.8×10^{-4} to 1.1×10^{-3} mol) was dissolved in 150 ml of spectral grade cyclopentane contained in a water-jacketed cylindrical Pyrex vessel. A quartz immersion well, containing a mercury resonance lamp, was placed into the photolysis vessel. The solution was deaerated with argon for about 1.5 hr before beginning the irradiation. Throughout the irradiation period the photolysis vessel was maintained at 25.0 ± 0.1° using a Bronwill Constant Temperature Circulator. After a photostationary state was obtained, as observed by periodic analysis of aliquots, the solution was analyzed and the ratio of the two isomers obtained.

Quantum Yields. Purified *cis*- and/or *trans*-1-phenyl-2-butene (130 mg, 9.8×10^{-4} mol) was added to 50 ml of spectral grade cyclopentane contained in Vycor glass tubes and deaerated for about 1.5 hr by bubbling argon through the solutions. Irradiation was supplied by the mercury resonance lamp using a rotating turntable (*cf.* Quenching Experiments). After the irradiation was complete, a known weight of internal standard was added, and the amount of the desired isomer of 1-phenyl-2-butene formed was determined. In each determination, the amount of product formed was corrected for back reaction by the method of Lamola.[28] In all quantum yield experiments no loss of 1-phenyl-2-butene was observed. The light intensity was determined during the irradiation of the 1-phenyl-2-butene solution by uranyl oxalate actinometry.

Quenching Experiments. Eight Vycor glass tubes (2.4 cm o.d. and 18.5 cm long) were filled with 50 ml of spectral grade cyclopentane and about 25 mg (1.89×10^{-4} mol) of purified *trans*-1-phenyl-2-butene. In the *trans*-2-hexene quenching experiments, varying amounts (0.17 to 1.09 g, 2.1×10^{-3} to 1.3×10^{-2} mol) of *trans*-2-hexene were added to six of the tubes. In the *cis*-piperylene experiments varying amounts (7.3 to 61 mg, 1.1×10^{-4} to 9.0×10^{-4} mol) of *cis*-piperylene were similarly added to six tubes. In both of the quenching studies two of the tubes served as standards with zero quencher concentration. The sample tubes were deaerated for at least 1 hr with argon after which time they were placed in a rotating turntable apparatus approximately equidistant from each other and approximately equidistant (4.0 cm) from a centrally located mercury resonance lamp situated in a quartz immersion well. The entire system, contained in a water-filled glass vessel, was maintained at 25.0 ± 0.2° using a Bronwill Constant Temperature Circulator. The turntable apparatus was constructed so that the tubes could be rotated around the centrally located lamp during irradiation. After allowing the tubes to come to thermal equilibrium with the bath, the samples were irradiated, and after irradiation a known weight of internal standard was added to each tube and the amount of *cis*-1-phenyl-2-butene formed was determined. The amount of the *cis* isomer formed was corrected for back reaction as previously mentioned and, in the piperylene experiments, correction was made for the amount of light absorbed by the *cis*-piperylene. When using *trans*-2-hexene as quencher no loss of 1-phenyl-2-butene was observed. In the *cis*-piperylene quenching experiments, 1-phenyl-2-butene was shown not to have disappeared except in the three samples which contained *cis*-piperylene in concentrations greater than 1.2×10^{-2} *M*. In these three samples the loss of 1-phenyl-2-butene was 1.5% or less.

Light Sources. For the photostationary state and quantum yield determinations a Hanovia low-pressure, mercury resonance lamp emitting at only 253.7 mμ was employed. The lamp itself was made from Vycor glass to remove the 184.9-mμ mercury resonance line.

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Intermediates in Anodic Oxidation of Carboxylates. Chronopotentiometry

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Abstract: Two steps are observed in chronopotentiometric oxidations of cesium salts of 2,2-dimethylpropanoic and 2,2-dimethylpentanoic acids on a platinum electrode in acetonitrile. The first step is a diffusion-controlled, one-electron oxidation; the second is not diffusion controlled and indicates that the product of the first step is partially lost in reactions not involving electrochemical oxidation. Acids less substituted on the 2 position show similar but less reproducible behavior.

The electrolysis of carboxylates is generally assumed to involve the intermediacy of both free radicals and in some cases carbonium ions.[2-11] The exact nature of the initial carboxylate–anode process, however, is not well understood.[12] The transient existence of alkyl carboxylate radicals ($RCO_2\cdot$) has generally been accepted despite the fact that alkyl carboxylate radicals from chemical processes have very short lifetimes (10^{-9} to 10^{-10} sec).[13] Most chemists concerned with anodic oxidation of carboxylates have assumed or have offered varying degrees of evidence that $RCO_2\cdot$ produced

$$RCO_2^- \text{ (solution)} \longrightarrow RCO_2\cdot \text{ (adsorbed)} + e^- \longrightarrow R\cdot \text{ (adsorbed)} + CO_2 \quad (1)$$

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