Mechanisms of Elimination Reactions. XXI. Ring-Size Effects and the Nature of the Excited States in the Photolysis of Cycloalkyl Phenylacetates[1]

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Abstract: Quantum yields for photoelimination and cis/trans ratios of the olefinic products were determined in the photolysis of a series of cycloalkyl phenylacetates (cyclopentyl through cyclododecyl). The profiles for quantum yields of cis and trans olefins *vs.* ring size were similar to the rate profiles *vs.* ring size for thermal decomposition of cycloalkyldimethylamine oxides. The differences in detail, however, were sufficient to indicate that the photochemical and thermal eliminations are not entirely analogous mechanistically. It is suggested that the quantum yield in the photoelimination is determined mainly by the ease of abstraction of the β hydrogen and by the partitioning of the resulting diradical between product formation and return to reactant. Studies of emission spectra and of quenching by piperylene and 4-methyl-2-pentene indicate that the photoelimination occurs predominantly or exclusively *via* a singlet state. Formation of saturated hydrocarbon and sensitized isomerization of the first-formed olefinic products are, however, triplet-state reactions.

Although the type II photoelimination of esters has been far less thoroughly investigated than that of ketones, it was first observed some time ago,[3-7] and has been the subject of a moderate number of recent investigations.[8-12] We have studied some general features of phenylacetate photolysis,[13] and the stereochemistry of photoelimination from some 2-methylcycloalkyl phenylacetates.[14]

In the present research we undertook to examine in greater detail the stereochemical requirements for photoelimination from esters by studying the photolysis of a series of cycloalkyl phenylacetates. Overall quantum yields of olefin production were determined along with trans/cis ratios of the resulting cycloolefins, thereby permitting the calculation of separate quantum yields for the formation of the cis and trans olefins. The results are given in Table I and Figure 1. The observed trans/cis ratios depend on photolysis times because of an ester-sensitized isomerization of the first-formed olefin (see below), but this complication could be avoided either by extrapolation to zero time or by quenching the isomerization with piperylene.

The largest quantum yield is that from cyclopentyl phenylacetate, indicating that the photoelimination is most favored when the β carbon–hydrogen and the α carbon–oxygen bonds are parallel or nearly parallel to each other. The lowest overall quantum yield is from cyclohexyl phenylacetate, where these bonds are nearly perfectly staggered. The more flexible larger rings, where these bonds are presumably somewhere between the eclipsed and staggered conformations, give intermediate values.

Table I. Quantum Yields in the Photolysis of Cycloalkyl Phenylacetates in Hexane at 254 nm[a]

Cycloalkyl	Φ_{elim}	Cis/trans olefin[b]	Φ_{cis}	Φ_{trans}
Cyclopentyl	0.127 ± 0.015		0.127	
Cyclohexyl	0.046 ± 0.002		0.046	
Cycloheptyl	0.056 ± 0.008		0.056	
Cyclooctyl	0.080 ± 0.003	1.20	0.044	0.036
Cyclononyl	0.081 ± 0.005	1.07	0.042	0.039
Cyclodecyl	0.113 ± 0.006	0.91	0.054	0.059
Cycloundecyl	0.105 ± 0.006	0.40	0.030	0.075
Cyclododecyl	0.052 ± 0.003	0.78	0.023	0.029

[a] See Experimental Section and ref 14 for details of procedures. [b] See Table II.

While detailed discussion of the results in the medium (7–12 carbons) rings is rendered difficult by their relative flexibility, a comparison with other reactions of known stereochemistry is instructive. This is the rate-profile technique used so effectively by Sicher and his coworkers.[15-17] In this technique, a plot of rate *vs.* ring size for the reaction in question is compared with plots for other reactions of known stereochemistry. An appropriate comparison for the photoelimination would be a thermal elimination known to occur by a syn cyclic mechanism, such as the thermal decomposition of cycloalkyldimethylamine oxides shown in Figure 2.[18] It is immediately evident that there are general similarities in shape between the quantum yield plots of Figure 1 and the rate plots of Figure 2, but there are also important differences. The relative magnitudes of the changes in quantum yields and rate are not always concordant, and the maxima in the plots occur at different ring sizes (at C-10 for trans olefin

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Partial support was also provided by the Center for Naval Analysis of the University of Rochester.

[2] Chas. Pfizer Fellow, 1969–1970.

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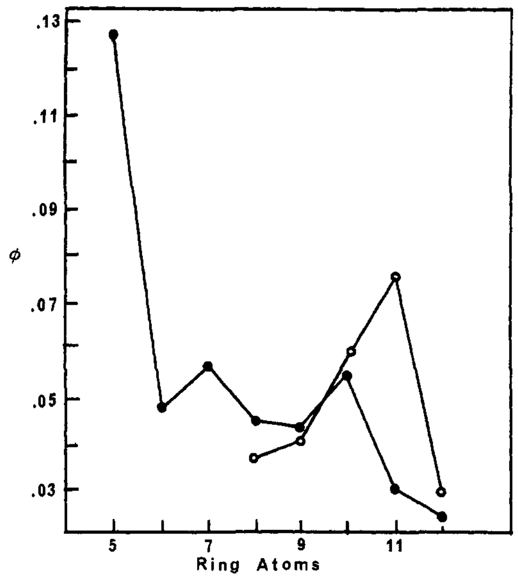


Figure 1. Effect of ring size on quantum yield of *cis*- and *trans*-cycloalkene in the photolysis of cycloalkyl phenylacetate in hexane at 254 nm: (●) cis and (○) trans cycloalkene.

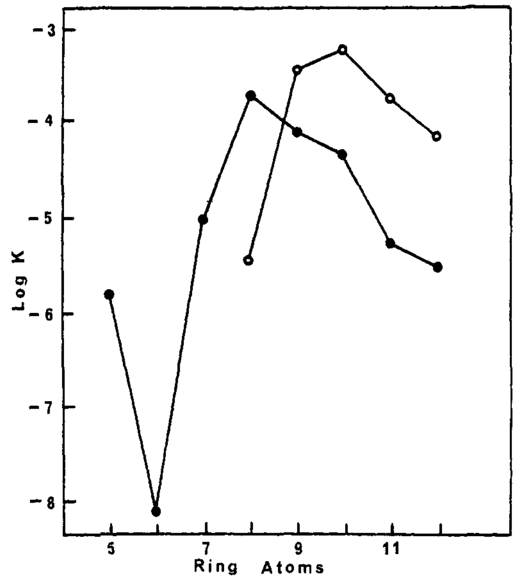


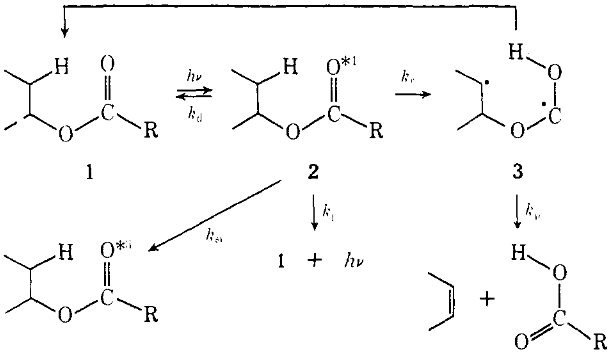
Figure 2. Effect of ring size on the rate of cis and trans cycloalkene formation from cycloalkyldimethylamine oxides in *tert*-butyl alcohol at 70.6°: (●) cis and (○) trans cycloalkene. Data from ref 18.

from the amine oxides, and at C-11 for trans olefin from the esters, for example).

If one assumes that both the thermal and photochemical eliminations are concerted processes, the only apparent rationales for such results would be that the five-membered-ring transition states for the amine oxides and the six-membered-ring transition states for the esters are affected in markedly different ways by the size of the cycloalkyl group or that the reactivity of the excited esters is somehow different from that of the ground-state amine oxides. Other evidence, however, strongly suggests that the photoelimination is a two-stage process with a biradical intermediate.[8,10,14] If this is the case, then the quantum yield may not be related in a simple fashion to the rate of abstraction of the β hydrogen by the oxygen of the excited carbonyl group.

The basis of this assertion can be appreciated from the mechanism of Scheme I. We assume in Scheme I that an excited singlet of the ester is the reactive species, a point which we will discuss below. The mechanism of Scheme I leads to the expression in eq 1 for the quantum yield of olefin in the photolyses, where γ is the efficiency with which the excited singlet, **2**, is populated, and the other terms are defined in Scheme I. Only if the quantum yield is controlled by the numerator (k_r) of the first term in brackets would one expect a close correlation of the profiles for the thermal and photochemical eliminations. The first term in brackets is very probably controlled by k_r, for the rates of the other processes which **2** can undergo should be little affected by ring size, and the low quantum efficiency suggests $k_r < k_r + k_d + k_{st} + k_f$. Similarly, γ should be independent of alkyl structure. There is, however, no reason why $k_p/(k_p + k_h)$ should either remain constant or vary in the same manner as k_r. In fact, the rate of return of hydrogen, k_h, should depend on conformation in much the same manner as k_r, and k_p should depend on the efficiency of overlap of the p orbital containing the unpaired electron on the β carbon with the α carbon–oxygen bond. The more efficient the overlap, the easier concerted carbon–oxygen cleavage and double bond formation from the diradical should be.[14] While it is hard to predict the net effect on $k_p/(k_p + k_h)$, it is certainly likely that it will contribute independently to Φ and thereby prevent Φ from simply reflecting changes in k_r.

Scheme I



$$\Phi = \gamma\left[\frac{k_r}{k_r + k_d + k_{st} + k_f}\right]\left[\frac{k_p}{k_p + k_h}\right] \qquad (1)$$

Perhaps the major difference between the ester photolysis and the amine oxide pyrolysis lies in the cis/trans ratios of the resulting olefin. These ratios do not vary greatly in the photolysis, remaining between 0.40 and 1.20 with most near unity (Table I), while in the pyrolysis of amine oxides the ratio is very large for cyclooctyl and then drops below 0.1 for cyclodecyl through cyclododecyl. Even in the pyrolyses of cyclodecyl acetate and xanthate, which are more closely related to the ester photolysis, the preference for trans olefin is marked (2:1 for the acetate and 6:1 for the xanthate).[19] These differences are best explained in terms of a two-stage mechanism for the photolysis with a diradical intermediate. The cis/trans ratio is de-

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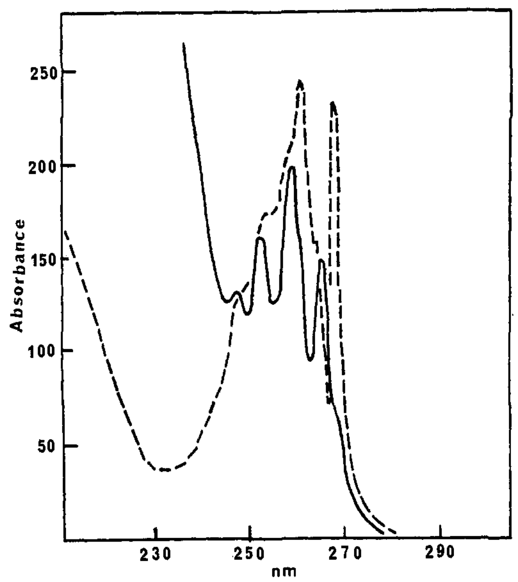

Figure 3. Ultraviolet absorption spectra of cyclohexyl phenylacetate (——) and an equimolar mixture of cyclopentyl acetate and toluene (----). Molar absorbance is plotted in each case.

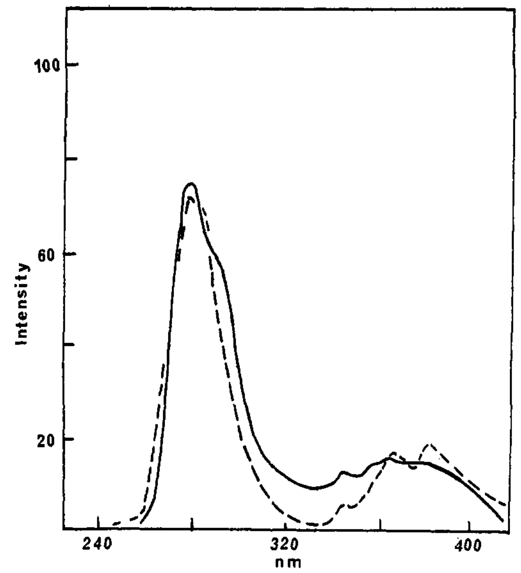

Figure 4. Total emission spectra at 77°K in 3-methylpentane glass of cyclooctyl phenylacetate (——) and toluene (----). Intensities are on an arbitrary scale and do not reflect relative intensities for the two compounds.

termined in the second step, decomposition of the biradical, which can be expected to have distinctly different stereochemical requirements from either the first-stage hydrogen abstraction or the concerted mechanism. Neither our cis/trans ratios nor those from the amine oxide pyrolysis[18] correlate well with the equilibrium ratios,[15] though ours are closer for cycloundecyl and cyclododecyl.

It should be emphasized that cis/trans ratios for finite extents of reaction do not reflect accurately the kinetically controlled ratio. While quantum yields for olefin formation are constant below *ca.* 10% conversion, cis/trans ratios are still not constant even at 3-4% conversion. The true values (Table II) can be obtained by extrapolation of values at different conversions to zero time, or by adding a small amount (0.008 *M*) of *cis*-piperylene to the reaction mixture. This high effectiveness at low concentration strongly suggests that triplets are being quenched. This conclusion is strengthened by three observations. First, piperylene is isomerized and on long photolysis gives the photostationary state.[20] Second, methyl phenylacetate sensitizes the isomerization of cyclodecene, the observed photostationary state being identical with that reported for benzene sensitization.[21] Finally, although piperylene does quench the photoelimination from cycloalkyl phenylacetates by what is believed to be singlet quenching (see below), cis/trans isomerization of the olefins is completely suppressed at piperylene concentrations that produce only slight quenching of photoelimination or fluorescence of the esters.

Table II. True Cis/Trans Rates for Cycloalkenes from Photolysis of Cycloalkyl Phenylacetates in Hexane at 254 nm

	Cis/trans ratios from	
Cycloalkene	Quenching[a]	Extrapolation[b]
Cyclooctene	1.20	
Cyclononene	1.07	1.39
Cyclodecene	0.91	0.91
Cycloundecene	0.40	0.34
Cyclododecene	0.78	0.85

[a] Photolysis in presence of 0.008 *M cis*-piperylene, which quenches all olefin isomerization. [b] Extrapolation to zero reaction of cis/trans ratios from reactions run to different per cent conversions.

We next sought to determine the nature of the excited state (or states) responsible for the photoelimination. The ultraviolet absorption spectrum of cyclohexyl phenylacetate is shown in Figure 3. For comparison, the figure also shows the spectrum of an equimolar mixture of cyclopentyl acetate and toluene. The spectrum of the mixture is almost identical with that of toluene, except for slightly greater intensity in the vicinity of 230 nm. By contrast, the spectrum of cyclohexyl phenylacetate shows much stronger absorbance below 230 nm and a similarity, but by no means identity, to that of toluene above 250 nm. The emission spectra of cyclooctyl phenylacetate and toluene, shown in Figure 4, are rather more similar. In particular, the fluorescence maxima (280 nm) are almost identical. The O–O band for phosphorescence of the ester was taken to be that at 346 nm, corresponding to a triplet energy of 83 kcal/mol. Our spectrum of toluene gives the same triplet energy, in agreement with the literature.[22] The intensity scales in Figure 4 are arbitrary and do not reflect relative intensities of the two spectra. A comparison of fluorescence intensities revealed that the ester fluorescence is about one-third the intensity of the toluene fluorescence.

The absorption and emission spectra reveal that the benzene and ester chromophores preserve their individuality to some extent, but also that there are significant interactions, in agreement with earlier observations on 2-ethoxyethyl phenylacetate.[11] In order to obtain further evidence on whether the mech-

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(20) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and J. C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

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anism of the photoelimination could be regarded as absorption of light by the benzene ring, followed by intramolecular energy transfer to the carbonyl group, we attempted *intermolecular* sensitization. Cyclopentyl and cyclohexyl acetates were photolyzed at 254 nm for 4 hr, both in benzene solvent and in hexane with equimolar amounts of ester and benzene. No olefin could be detected. Attempted sensitization of cyclooctyl phenylacetate photolysis in benzene or acetone at 300 nm, and with benzophenone, acetophenone, or cyclopropyl phenyl ketone in benzene at 300 and 366 nm likewise failed. No ester was consumed and no olefin formed. Intermolecular energy transfer is obviously very inefficient. The direct photolysis of the phenylacetates either is not properly described as involving an intramolecular energy transfer, or else the efficiency of the intramolecular transfer is markedly enhanced by the proximity of the chromophores.

Both the fluorescence and the chemical reactions of the phenylacetates were quenched by *cis*-piperylene. The quenching followed the Stern–Volmer relationship (eq 2), where Φ is the quantum yield in the presence, and

$$\Phi^0/\Phi = 1 + k_q\tau_s[\mathrm{Q}] \qquad (2)$$

Φ^0 in the absence of quencher, k_q is the rate constant for quenching, τ_s the lifetime of the state being quenched, and [Q] the piperylene concentration. The slopes, $k_q\tau_s$, of the plots are recorded in Table III.

Table III. The Slopes, $k_q\tau_s$, of Plots of Φ^0/Φ *vs.* Piperylene Concentration[a]

Compd	Process quenched	$k_q\tau_s$
Toluene	Fluorescence	38.7 ± 1.3
Cyclohexyl phenylacetate	Fluorescence	21.8 ± 0.7
Cyclodecyl phenylacetate	Fluorescence	23.2 ± 0.7
Cycloundecyl phenylacetate	Fluorescence	25.9 ± 0.9
trans-2-Methyl-cyclohexyl phenylacetate	Fluorescence	22.2 ± 0.8
Cyclodecyl phenylacetate	Olefin formation[b,c]	46
Cyclodecyl phenylacetate	Ester loss[b,d]	130

[a] Photolysis at 254 nm in hexane, ester concentration 0.025–0.035 *M*, piperylene concentration ranges ran from 0–0.08 to 0–0.20 in the fluorescence quenching. Solutions were not degassed unless otherwise noted. [b] Samples degassed. [c] Piperylene concentration 0–0.018 *M*. [d] Piperylene concentration 0–0.012 *M*.

If the rate of quenching, k_q, is the same for all of the compounds, then the fluorescence quenching studies indicate that the lifetimes of the ester singlets are all very similar to each other, but only *ca.* 55–65% of the lifetime of the toluene singlet. As noted above, the fluorescence of the esters is very similar to that of toluene but only about one-third as intense. Thus, there is obviously a nonradiative decay path for the phenylacetate singlets which is not available to, or slower for, the toluene singlet. Likely candidates would be intersystem crossing, direct chemical reaction, or intramolecular energy transfer. The first can be excluded, for the quantum yields for intersystem crossing are less for cyclooctyl (0.15) and cyclodecyl (0.21) phenylacetates than for toluene (0.55), as determined by the method of Lamola and Hammond.[23] The second is unlikely, for the ester singlet lifetimes should then vary with the varying ease of photoelimination, instead of remaining nearly constant. We conclude that intramolecular energy transfer from phenyl singlet to ester singlet is the most likely extra decay path for the phenylacetate singlets.

The fact that the slope for quenching of olefin formation is about twice that for quenching of fluorescence could indicate that some olefin arises from a state (probably triplet) more easily quenched than the fluorescing singlet. On the other hand, the chemical reactions were performed in degassed tubes, while the fluorescence cells could not be degassed. It is more probable that the fluorescence was partially quenched by dissolved oxygen, and that the apparent difference in slopes is merely an artifact.

The same explanation cannot apply to the difference in slopes for quenching of olefin appearance and ester loss, for both were run in degassed tubes. Although the plots showed some scatter and a rather narrow range of piperylene concentrations was used, there is no doubt that the slopes are different. Ester loss from some excited state other than that which leads to photoelimination is suggested. We know that some cycloalkyl phenylacetates give saturated hydrocarbons on photolysis.[14] Although cyclodecane was not found among the products from cyclodecyl phenylacetate, it and other radical-derived products were not carefully sought and may have been present. A problem in this interpretation is that ester loss *via* both singlet and triplet states would probably yield a curved Stern–Volmer plot with piperylene,[24] and ours is straight from 0 to 0.012 *M* piperylene. Unfortunately, we could not go to higher piperylene concentrations because of appreciable light absorption by the piperylene.

When cyclooctyl and cyclodecyl phenylacetates are photolyzed in the presence of 0–0.16 *M* *cis*-4-methyl-2-pentene, the cis/trans ratios of the cycloalkenes are lowered, but the overall quantum yield of cycloalkene formation is unaffected. The *cis*-4-methyl-2-pentene is isomerized. *cis*-4-Methyl-2-pentene has no effect on the fluorescence of toluene or the cycloalkyl phenylacetates in the concentration range used. Evidently the 4-methyl-2-pentene is suppressing triplet-sensitized isomerization of the cycloalkenes, just as does piperylene (see above). The absence of an effect on the photoelimination suggests again that the elimination products come from the singlet state.

In order to determine whether the ester triplet was involved in processes other than olefin isomerization, a careful study was made of the products from *trans*-2-methylcyclohexyl phenylacetate[14] in the presence of 4-methyl-2-pentene. The effects on the quantum yields of the various products are outlined in Table IV. We have noted in the accompanying paper[14] that methylenecyclohexane results from a triplet-sensitized isomerization of 1-methylcyclohexane. This process is rather efficiently quenched by 4-methyl-2-pentene. Aside from this artifact, neither olefin composition nor total quantum yield of olefins is affected by 4-methyl-2-pentene, again indicating that the methylcyclohexenes arise from a singlet state. Methylcyclohexane forma-

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[23] A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965).
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Table IV. Quantum Yields in Photolysis of *trans*-2-Methylcyclohexyl Phenylacetate in Hexane at 254 nm in the Presence of *cis*-4-Methyl-2-pentene

Product	Φ at [4-methyl-2-pentene] × 10^3 of 0	32	64	96	160	320
Methylcyclohexane	0.014		0.012	0.010	0.009	0.007
Methylenecyclohexane	0.007	0.001	0.001	0.001	0.000	0.000
1-Methylcyclohexene	0.010	0.011	0.014	0.015	0.013	0.013
3-Methylcyclohexene	0.014	0.014	0.017	0.017	0.013	0.015
Total olefin	0.030	0.026	0.032	0.033	0.026	0.028
Total products	0.044		0.043	0.043	0.037	0.036

tion is quenched distinctly less efficiently than is methylenecyclohexane formation. Furthermore, the isomerization of *cis*-4-methyl-2-pentene by the ester triplets is also much more efficient than the quenching of methylcyclohexane formation. This suggests that the same excited state is not involved in both processes. Possibly triplet excitation centered on the phenyl group of the phenylacetate is responsible for the sensitized isomerization, while triplet excitation centered on the ester group (and formed *via* intersystem crossing from singlet excited ester) is responsible for the saturated hydrocarbon and other radical-derived products.

Experimental Section[25]

Alcohols. Those alcohols which were commercially available and their sources are as follows: cyclopentanol and cyclohexanol (Eastman Organic Chemicals); cycloheptanol, cyclooctanol, and cyclododecanol (Aldrich Chemical Co.). The remaining alcohols were prepared as described below.

Cyclononanol was obtained by reduction of cyclononanone in methanol by the dropwise addition of a 50% excess of sodium borohydride in 20% water in methanol. The methanol was removed by distillation, the residue was extracted with ether, and the extracts were dried over magnesium sulfate. Fractionations yielded material of bp 55° (0.6 mm) (lit.[26] bp 115–119° (15 mm)). The cyclononanone was prepared by dehydroxylation of azeloin with zinc in acetic acid.[27] The azeloin in turn resulted from the acyloin condensation of diethyl azelate (Aldrich Chemical Co.)[28]

Cyclodecanol was prepared by reduction of cyclodecanone in the same manner as described above for cyclononanone, bp 118–119° (10.5 mm), mp 39.8–41.5° (lit.[29] bp 125° (12 mm), mp 40–41°). The cyclodecanone was obtained, as above for cyclononanone by dehydroxylation of sebacoin,[27] which in turn resulted from the acyloin condensation of dimethyl sebacate (Eastman Organic Chemicals).[28]

Cycloundecanol was prepared by reduction of cycloundecanone as described above for cyclononanone, bp 70° (1 mm) (lit.[29] bp 128–131° (20 mm)), phenylurethane, mp 57.5–58° (lit.[29] bp 59°). The cycloundecanone was obtained by treatment of *cis*-2,12-dibromocyclododecanone with sodium methoxide in xylene, followed by treatment of the product with sodium azide and concentrated sulfuric acid.[30] The *cis*-2,12-dibromocyclododecanone was obtained by bromination of cyclododecanone (Aldrich Chemical Co.).[30]

Phenylacetate esters were prepared by the procedure described in the accompanying paper.[14]

Cyclopentyl phenylacetate had bp 100–110° (0.1 mm). *Anal.* Calcd for $C_{13}H_{16}O_2$: C, 76.47; H, 7.84. Found: C, 76.32; H, 7.92. Purity by glpc >99%.

Cyclohexyl Phenylacetate. See accompanying paper for properties and analysis.[14]

Cycloheptyl phenylacetate had bp 123–125° (0.1 mm). *Anal.* Calcd for $C_{15}H_{20}O_2$: C, 77.59; H, 8.62. Found: C, 77.53; H, 8.47. Purity by glpc 97%.

Cyclooctyl phenylacetate had bp 115° (0.05 mm). *Anal.* Calcd for $C_{16}H_{22}O_2$: C, 78.05; H, 8.94. Found: C, 78.11; H, 9.17. Purity by glpc 99%.

Cyclononyl phenylacetate had bp 150° (0.25 mm). *Anal.* Calcd for $C_{17}H_{24}O_2$: C, 78.46; H, 9.23. Found: C, 78.72; H. 9.18. Purity by glpc 99%.

Cyclodecyl phenylacetate had bp 146–150° (0.1 mm). *Anal.* Calcd for $C_{18}H_{26}O_2$: C, 78.83; H, 9.49. Found: C, 78.85; H, 9.66. Purity by glpc 99%.

Cycloundecyl phenylacetate had bp 155–158° (0.3 mm). *Anal.* Calcd for $C_{19}H_{28}O_2$: C, 79.17; H, 9.72. Found: C, 79.38; H, 9.77. Purity by glpc >99%.

Cyclododecyl phenylacetate had mp 36–38° *Anal.* Calcd for $C_{20}H_{30}O_2$: C, 79.47; H, 9.93. Found: C, 79.38; H, 9.93. Purity by glpc >99%.

Acetate esters were prepared by the same procedure as the phenylacetates,[14] except that acetyl chloride was used instead of phenylacetyl chloride.

Cyclopentyl acetate had bp 150–151° (lit.[31] bp 153°). The material showed only one component by glpc.

Cyclohexyl acetate had bp 30–31° (1 mm) (lit.[31] bp 172° (752 mm)). Purity by glpc 98%.

Olefins. Those olefins which were available and their sources are as follows: cyclopentene and cyclohexene (Chemical Samples Co.); cyclodecene (kindly furnished by Dr. D. S. Bailey). The remaining olefins were prepared as described below.

Cycloheptene. A mixture of 20 g (0.18 mol) of cycloheptanol (Aldrich Chemical Co.) and 5 ml of 85% phosphoric acid was refluxed for 8 hr and then distilled. The water was removed in a separatory funnel, and the olefin was dried over magnesium sulfate. Fractionation yielded material of bp 112°, n^{25}D 1.4556 (lit.[32] bp 112–113°, n^{20}D 1.4580).

Cyclooctene was prepared in the same manner as cycloheptene, bp 139–141°, n^{25}D 1.4667 (lit.[33] for *cis*-cyclooctene, bp 65° (59 mm), n^{25}D 1.4682). Purity 97% by glpc. Only the cis isomer was obtained, as shown by its ir spectrum.

Cyclononene was prepared in the same manner as cycloheptene, bp 165–166° (lit.[26] for *cis*-cyclononene, bp 167–169°). Purity by glpc 98%. Only the cis isomer was obtained, as shown by glpc and ir spectrum.

Cycloundecene was prepared by heating the *p*-toluenesulfonate (prepared in the usual manner[34]) of cycloundecanol for 9 hr at 100° in dimethylformamide in a sealed stainless-steel tube. The solution was poured into water and extracted with pentane. The extract was washed with 10% sulfuric acid and water, and dried over magnesium sulfate. Finally, it was treated with 2 g of Woelm grade I alumina for 5 min, and the pentane was removed on a rotary evaporator. The infrared spectrum of the residue was identical with that of known *trans*-cycloundecene.[35]

Cyclododecene was prepared by the solvolysis of the *p*-toluenesulfonate[34] of cyclododecanol in the same manner as for cycloundecene. The product was equilibrated in a stainless-steel tube at 130° for 288 hr with a little 0.05 *M* *p*-toluenesulfonic acid

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(25) Melting points are corrected; boiling points are not. Microanalyses by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Chemalytics Inc., Tempe, Ariz.

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in acetic acid.[36] The crude product was coinjected on glpc with known cyclododecene (Aldrich Chemical Co). and showed two components in a ratio of 0.55. Since the reported equilibrium cis/trans ratio is 0.53,[36] the larger peak was assigned to *trans*-cyclododecene.

Identification of Cis and Trans Cycloalkanes. Cyclooctene. Photolysis of cyclooctyl phenylacetate in hexane at 254 nm gave a two-component product mixture on a 6 ft × 0.25 in. 25% Emulphor-O column at 95°. The mass spectrum of the mixture was identical with that of known *cis*-cyclooctene (above), and one of the peaks was coinjected with known *cis*-cyclooctene. The other was assumed to be *trans*-cyclooctene.

Cyclononene. Photolysis of cyclononyl phenylacetate in the same manner as for cyclooctene gave two peaks upon glpc analysis on the same Emulphor-O column, one of which was identical with that for known *cis*-cyclononene (above). The other was assumed to be *trans*-cyclononene.

Cyclodecene was converted to the photostationary state (83% cis and 17% trans) as described in the literature.[21] The resulting two peaks were coinjected with those obtained on photolysis of cyclodecyl phenylacetate.

Cycloundecene. Photolysis of cycloundecyl phenylacetate gave two peaks upon glpc analysis, one of which coinjected with known *trans*-cycloundecene (above).

Cyclododecene. Identification of the cis and trans isomers is described above under the preparation of cyclododecene.

Analysis by glpc followed the procedures of the accompanying paper.[14] The columns used (all $^1/_8$ in. diameter) for the various products, along with the conditions, were as follows: a 20-ft column of 15% silver nitrate in ethylene glycol on firebrick (Varian) for cyclopentene and cyclohexene (50°, 54 psi); a 10-ft column of 12% Emulphor-O (Applied Science) on firebrick (Varian) for cycloheptene (85,° 40 psi), *cis*- and *trans*-cyclooctene (110°, 60 psi), and cyclodecyl phenylacetate (160°, 52 psi); a 6-ft column of 10% Carbowax 20M-PTA (Applied Science) on Anakrom ABS (Analabs) for *cis*- and *trans*-cyclononene and *cis*- and *trans*-cyclodecene (65°, 26 psi); a 20-ft column of the same material for *cis*- and *trans*-cyclononene (75°, 56 psi); a 5-ft column of 25% TCEP (Applied Science) on firebrick (Varian) for *cis*- and *trans*-cycloundecene (75°, 20 psi), and *cis*- and *trans*-cyclododecene (80°, 44 psi); a tandem column of 10 ft of silver nitrate in triethylene glycol on Chromosorb P followed by 6 ft of tricresyl phosphate (Burrell) on Chromosorb P for *cis*- and *trans*-piperylene (ambient temp, 56 psi); and a tandem column of 12 ft of 20% 2 N $AgNO_2$ in ethylene glycol on Chromosorb P followed by 3 ft of tricresyl phosphate (Burrell) on Chromosorb P for *cis*- and *trans*-4-methyl-2-pentenes (ambient temperature, 40 psi).

Photolysis Procedures. The basic procedures were the same as those described in the accompanying paper.[14] Irradiations at 254 nm used unfiltered light from the Rayonet RUL 2537 lamps. Irradiations at 300 nm utilized the Rayonet RUL 3000 lamps with removal of light below 290 nm by use of Kimax tubes. Irradiations at 366 nm utilized the Rayonet RUL 3500 lamps and a metal merry-go-round apparatus in which the sample tubes were rotated behind stationary windows fitted with $3^1/_8$ in. × $3^1/_8$ in. Corning 7-60 blue filters and 3-94 uranium glass filters.

Cis/Trans Ratios of Cycloalkenes. The true cis/trans ratios for cyclooctene through cyclododecene were determined by photolyzing each ester at 0.025–0.035 M in hexane in degassed tubes with 0.008 M *cis*-piperylene, which was shown to quench all olefin isomerization. The ratios so obtained are compared in Table II with those from extrapolation of ratios from different per cent conversions to zero time.

Quenching Experiments. These were conducted in the same manner as the other direct photolyses. Hexane solutions of the appropriate phenylacetate and the quencher, *cis*-piperylene or *cis*-4-methyl-2-pentene, were placed in quartz tubes, degassed, and photolyzed. Quantum yields were corrected for the small amount of competitive light absorption by *cis*-piperylene. Isomerization of the quencher cis olefins was corrected for back reactions of the trans olefins.[23]

Attempted Sensitized Photolyses of Esters. Cyclooctyl phenylacetate and acetophenone, benzophenone, or cyclopropyl phenyl ketone were dissolved in benzene, degassed, and photolyzed at 366 nm. Cyclooctyl phenylacetate was also photolyzed in acetone at 300 nm and in benzene at 254 and 300 nm. No olefin was formed or ester lost at ester concentrations of 0.03–0.17 M and reaction times of 15–216 hr.

Cyclohexyl acetate in benzene gave no products when irradiated for up to 4 hr. Similarly, 0.035 M cyclopentyl acetate and 0.167 M benzene in hexane gave no products at 254 nm after 4 hr.

A mixture of 0.030 M cyclopentyl acetate and 0.034 M methylphenylacetate in benzene gave no product at 254 nm after 4 hr.

Fluorescence spectra were determined using a Perkin-Elmer MPF-2A fluorescence spectrophotometer. The light source for excitation was a Perkin-Elmer 150 W xenon lamp with a Model 150 Xenon lamp power supply. The detector was a HTV Type R106 photomultiplier (Hamamatsu TV Co., Japan) located at a right angle to the direction of the incident light. The recorder was a Hitachi QPD-33 electronic recorder.

Solutions were contained in 1.0-cm quartz cells, and were adjusted in concentrations to have absorbances of 0.80–1.20 (usually about 1.0) so as to assure maximum fluorescence intensity and to obviate the need for corrections for differences in absorbance (the maximum in a fluorescence intensity *vs.* absorbance plot, determined by Dr. F. C. Montgomery, occurs in this range). Cells were not degassed, and were allowed to reach thermal equilibrium in the cell compartment before the spectra were measured. The exciting wavelength was 266 nm. Spectra were not corrected for photomultiplier response or wavelength-dependent factors in the instrument's optical path.

Fluorescence Quenching. The *cis*-piperylene used was transferred bulb-to-bulb on a vacuum line at least three times prior to each use, and was shown to be >99% pure by glpc. Variations of ester or toluene concentration between 0.0013 and 0.060 in hexane did not affect the fluorescence quenching. A correction was made for the small amount of competitive absorption by the *cis*-piperylene at the wavelength of excitation (266 nm).

Total emission and phosphorescence spectra were determined using the Perkin-Elmer MPF-2A spectrophotometer equipped with a variable speed rotating chopper for phosphorescence spectra. The samples were contained in a 0.1-cm quartz cell immersed in a quartz liquid nitrogen trap. The solvent used to form the glass at 77°K was 3-methylpentane purified according to Parker.[37] The exciting wavelength was 263 nm for the esters and 266 nm for toluene. Again, no corrections were made for the wavelength response of the instrument.

Quantum efficiencies for intersystem crossing were determined by the method of Lamola and Hammond[23] using 4-methyl-2-pentene as the triplet quencher. The quantum yield of isomerization of 4-methyl-2-pentene was independent of olefin concentration at the higher concentrations, and was corrected for back reaction. The photostationary state for the sensitized isomerization of 4-methyl-2-pentene was found to be 54% trans and 46% cis by irradiation of some samples until no further change was observed. Irradiations were in degassed quartz tubes. From plots of $1/\phi_{\mathrm{isom}}$ *vs.* 1/[4-methyl-2-pentene], ϕ_{st} was determined from the intercepts.

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