

Mechanism of Photoreactions of Phenylketene Acetals

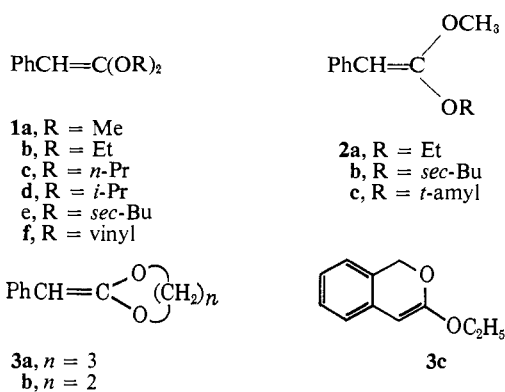
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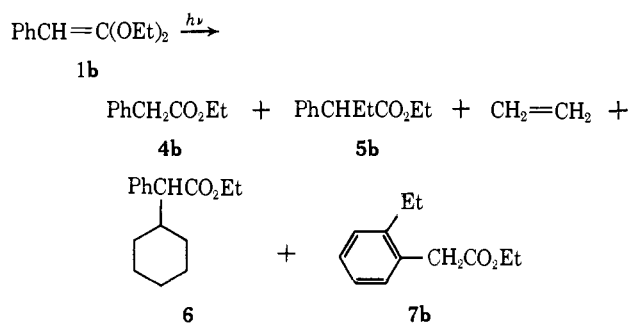
Abstract: Quantitative investigations of the photoreactions of phenylketene acetals have shown that the observed molecular rearrangements are intramolecular; a linear relationship between the logarithm of relative quantum yields for photolytic decomposition of phenylketene dialkyl acetals and the bond-dissociation energy D_{R-H} , where R corresponds to the alkyl group in the acetal, exists; product distributions but not quantum yields change with solvent; and product ratios are sensitive to the alkyl groups in the dialkyl acetals. All these data are interpreted in terms of a single mechanism for those photoreactions which give rearrangements and fragmentations: homolytic decomposition of a C–O bond in a phenylketene acetal gives a pair of radicals which recombine, disproportionate, or react with solvent.

Quantitative investigations of the chemistry of ketene acetals have been hampered in the past both by synthetic difficulties and by inadequate physical methods. Typically, the synthetic methods used² would give material of uncertain purity, and physical techniques capable of quantitative detection of impurities or reactions such as hydrolysis,² competitive with a reaction under investigation, were not available or were not employed. Only a few ketene acetals in a series were available, thus precluding systematic study of substituent effects on chemical reactivity.

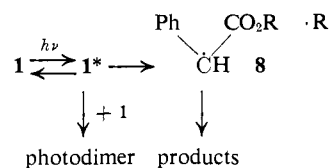
The developments in chemically useful instrumentation in the past two decades have substantially reduced one obstacle impeding quantitative scrutiny of the chemistry of ketene acetals (and other comparatively unstable molecules), and extension of synthetic routes to phenylketene acetals through dehydrobromination of α -bromophenylacetaldehydes³ has provided a wide variety of these ketene acetals (1–3) in reasonable and known purities, thus removing the other.



A thorough study of the products derived from most of these phenylketene acetals through photolyses in cyclohexane has established the general course followed in the photolytic decompositions.⁴ In a representative photolysis, the diethyl acetal **1b** was converted to ethyl phenylacetate (**4b**), ethyl α -phenylbutyrate (**5b**), ethylene, ethyl phenylcyclohexylacetate (**6**), ethyl *o*-ethylphenylacetate (**7b**), and a photodimer. From the



spectrum of products observed it seemed possible that the rearrangement and fragmentation products stemmed from an initially formed pair of radicals (**8**), and that the photodimer was produced in a process competitive with deactivation and homolysis of **1***.



But mechanistic ambiguities remained. The postulated radicals in **8** might be efficiently caged by solvent or free to react intermolecularly with other molecules or able to propagate radical chains. A concerted cyclo-reaction pathway for formation of an alkyl phenylalkylacetate from **1** might be competitive with the formation of a product of this type from the radical pair **8**.

Results and Discussion

Quantitative experiments of four types designed and conducted to clarify these mechanistic possibilities are now described and evaluated. The observed intramolecularity of the rearrangement reactions, relative insensitivity of quantum yield for photodecomposition of phenylketene dialkyl acetals to the identity of the alkyl groups, solvent effects on quantum yields and product distributions, and variations in product distributions with the alkyl groups of the acetals **1** all proved consistent with a caged-radical mechanism for the rearrangement and fragmentation reactions.

Crossover Experiment. To secure a quantitative measure of the intramolecularity or intermolecularity of the rearrangement reactions of the phenylketene

(1) National Science Foundation Cooperative Graduate Fellow, 1963–1966.

(2) S. M. McElvain, *Chem. Rev.*, **45**, 453 (1949).

(3) J. E. Baldwin and L. E. Walker, *J. Org. Chem.*, in press.

(4) J. E. Baldwin and L. E. Walker, *J. Am. Chem. Soc.*, **88**, 3769 (1966).

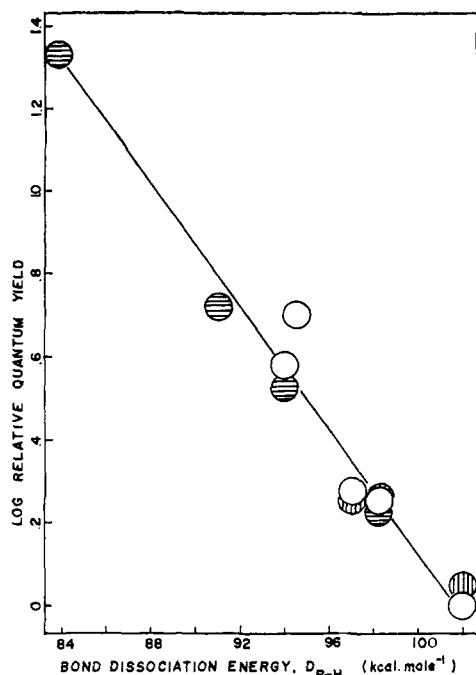


Figure 1. Log of relative quantum yield *vs.* D_{R-H} for photodecomposition of phenylketene dialkyl acetals. The open circles are experimental points, based on ultraviolet spectroscopic analyses. The vertically lined circles are based on vpc analyses. The horizontally lined circles are calculated (*cf.* Table I and text).

acetals, the mixed acetal **2a** was photolyzed. From phenylketene ethyl methyl acetal (**2a**) intramolecular rearrangements might give several products but none having a molecular weight higher than that of the starting material (178). An intermolecular mechanism for the rearrangement, however, would permit an alkyl group from one molecule of the starting material to combine with the carbalkoxybenzyl moiety of another, and ethyl α -phenylbutyrate (*m/e* 192) would be expected in the mixture of products.

The experimental results showed that the ethyl methyl acetal **2a**, contaminated by $4.6 \pm 1\%$ of the diethyl acetal **1b** (analysis by vpc), gave, on photolysis in cyclohexane, a mixture of products containing $4.5 \pm 0.5\%$ of ethyl α -phenylbutyrate (analysis by mass spectrometry). A statistical distribution corresponding to a completely intermolecular reaction would have given 32.4% ⁵ of ethyl α -phenylbutyrate. The phenylketene diethyl acetal (**1b**) in the mixed acetal **2a** was introduced in one of the synthetic steps.

The results from the crossover experiment demonstrate that the rearrangement leading to the alkyl phenylalkylacetates is intramolecular. If homolytic decomposition of a photoexcited phenylketene acetal gives a pair of radicals, they either recombine with one another, disproportionate, or react with solvent. A concerted or a cage-radical reaction mechanism for the rearrangement can accommodate the data. A chain-radical formulation cannot.

Relative Quantum Yields for the Photolyses of Phenylketene Acetals. Relative quantum yields for the disappearance of 11 phenylketene or phenylketene-type

(5) This figure represents the per cent of esters with *m/e* 178 or 192 having *m/e* 192; the relative rates of bond cleavage discussed in the following section as well as obvious statistical factors must be considered to calculate it.

acetals were obtained, following the progress of the photoreactions by periodically scanning diluted aliquots from the reaction mixture in the ultraviolet. The extinction coefficients for the compounds were obtained for each using the unirradiated solutions. For some of the less stable ketene acetals, where pure samples could not be obtained, a value of 16,000 was used for the extinction coefficients. This estimated value was selected both on the basis of calculations allowing for purities estimated from nmr spectra and of comparisons with values (16,000–17,000) of other related compounds that could be obtained pure. Beer's law was found to hold for all compounds encountered in this work; the absorption value for a given sample could be converted to concentration with appropriate factors. The rate of change of concentration for a given run was found from the slope of the concentration *vs.* time plot. Since some dark reaction was observed from slight leakage of moisture into the reaction tube, particularly on very humid days, the appropriate factor was subtracted from the observed rate. The Vycor tubes used for the relative quantum yield work varied in thickness by as much as 20%. The observed rates of reaction were corrected for "tube factors" obtained from the ultraviolet spectrum of each tube. To convert the resulting rates to relative rates (or relative quantum yields), the rate for the dimethyl acetal was assigned the relative rate of 1. Since the output of the lamp decreased with age, the values of all the rates decreased accordingly. Fortunately the lamp was sufficiently stable so that one unity value could be taken for a series of reactions run all together or closely following one another. The kinetic work was carried out in three groups of runs which were separated from one another by 1 to 2 months.

The relative quantum yields for photolytic decomposition of the phenylketene acetals in cyclohexane are summarized in Table I. These data and bond-dissocia-

Table I. Relative Quantum Yields for Photodecomposition of Phenylketene Acetals

Compd	R or <i>n</i>	Φ_r^a	Runs ^b	Φ_r (calcd)
1a	Me	1.00	18	
b	Et	1.81	7	1.69 ^c
c	<i>n</i> -Pr	1.86	15	
d	<i>i</i> -Pr	5.0 ± 0.3	3	
e	<i>sec</i> -Bu	3.8 ± 0.3	3	3.36 ^d
f	Vinyl ^e			
g	<i>t</i> -Amyl			5.3 ^f
h	Benzyl			21.5 ^g
2a	Et	1.43	6	
b	<i>sec</i> -Bu	2.82	12	
c	<i>t</i> -Amyl	4.6 ± 0.2	3	
3a	3	5.3 ± 0.2	3	
b	2	9.8 ± 0.6	2	
3c ^h		20 ± 1.3	3	

^a Relative quantum yields in cyclohexane at 25° determined by ultraviolet spectroscopy. ^b No more than three determinations of one compound run simultaneously. ^c Calculated from the relative quantum yields of **1a** and **2a**. ^d From data for **1a** and **2b**. ^e See Experimental Section. ^f From data for **1a** and **2c**. ^g From data for **1b** and **3c**. ^h The products from the decomposition of this acetal have not been determined.

tion energies from the literature are compared in Figure 1, where the logarithm of relative quantum yield, $\log \Phi_r$, is plotted against the bond-dissociation energy,

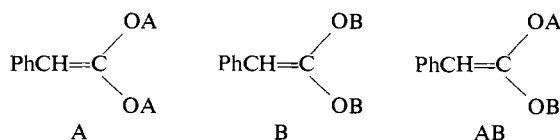
D_{R-H} , appropriate to the R group of the symmetrical acetals **1**. Relative quantum yields for four of the acetals determined by vpc analyses are given in Table II; the agreement between the two analytical methods is satisfactory. Although phenylketene acetals are known to be thermally unstable,⁶ the rate of decomposition is low enough to make vpc analyses feasible.

Table II. Solvent Effects on Relative Quantum Yields for Photodecomposition of Phenylketene Acetals

Compd	R	Solvent	Φ_r^a	Runs
1a	Me	Cyclohexane	1.12	1
		Cumene-cyclohexane ^b	1.01	1
b	Et	Cyclohexane	1.81 ^c	4
		Cumene-cyclohexane ^b	1.84	2
		1-Methylcyclopentene	1.76	2
c	<i>n</i> -Pr	Cyclohexane	1.75	1
d	<i>i</i> -Pr	Cyclohexane	3.2-4.3	1
2a	Et	Cyclohexane	1.49	2

^a Relative quantum yields at 25° determined by vpc analyses. ^b 15% cumene in cyclohexane. ^c Selected as standard value for comparisons.

A relationship between the relative rate of photodecomposition of an acetal AB having two different R groups and the rates of photodecomposition of the two acetals A and B each having both R groups identical and identical with one of the R groups in AB was required; this relationship permits inclusion of experimental data on Φ_r for the mixed acetals AB in the linear free-energy plot of Figure 1. The necessary derivation may be developed as shown below.



Let the relative rates of photodecomposition of acetals A, B, and AB be X , Y , and Z . Assume that the rate of breaking an O-A bond, in either A or AB, or of an O-B bond in B or AB, is independent of the other group (B or A) in the molecule. Consider now the separate reactions of A and B for a given time. The fraction of bonds broken during this time which are O-A bonds is given by $X/(X + Y)$ while the fraction of O-B bonds cleaved is $Y/(X + Y)$. For the acetal AB, the rate of photodecomposition is a composite of two reactions, since either an O-A or an O-B bond may be broken. The rate at which O-A bonds in AB are broken is X , and the fraction of O-A bonds broken is $X/(X + Y)$; thus the rate at which AB decomposes with cleavage of an O-A bond is $X^2/(X + Y)$, and the total relative rate of decomposition of AB is $[(X^2 + Y^2)/(X + Y)] = Z$. Solution of this equation for Y gives $Y = [Z + \sqrt{Z^2 + 4XZ} - 4X^2]/2$. Using this expression and experimentally accessible rate data, as for the dimethyl acetal **1a** and the methyl *t*-amyl acetal **2c**, one can calculate the rate of photodecomposition of the unavailable phenylketene di-*t*-amyl acetal (**1g**). Wherever all three compounds in a set A, B, and AB were available, the observed rates and the deduced

(6) S. M. McElvain and C. L. Stevens, *J. Am. Chem. Soc.*, **68**, 1917 (1946).

theoretical relationship among them were in fair agreement (Table I).

The bond-dissociation energies for the breaking of carbon-to-hydrogen bonds in hydrocarbons were selected from the literature.⁷ Most of the values reported are accurate at best to ± 1 kcal mole⁻¹. For the plot in this paper, the following bond-dissociation energies (kcal mole⁻¹) are used (R, D_{R-H}): Me, 102; Et, 98; *n*-Pr, 97; *i*-Pr, 94.5; *sec*-Bu, 94; *t*-amyl, 91; and benzyl, 84.

The cyclic acetals **3a** and **3b** decompose photolytically faster than would be predicted from the correlation of Figure 1. Since 2-benzylidenedioxolane (**3b**), which shows the greatest deviation from the correlation, is known to give a substantial yield of a photodimer while the acetals **1** do not, this rate behavior is not entirely unexpected.

The plot of Figure 1 shows a good linear correlation, indicative of a common rate-limiting step in the photolytic decompositions of the phenylketene dialkyl acetals. The small slope of the plot implies that the rates of photochemical decomposition of the phenylketene acetals **1** are fairly insensitive to the character of the O-R bond broken. Some superficially analogous processes, photodecomposition of tertiary hypohalites⁸ and thermal decarbonylation of aldehydes,⁹ give linear $\log k_r$ vs. D_{R-H} plots with much larger slopes. For the photochemical decomposition of the hypohalites at 40°, the relative rates for breaking the R-C bond in the alkoxy radical (R-CMe₂CO·) for R's equal to Me, Et, *i*-Pr, and *t*-Bu are, respectively, 0.01, 1, 36, and >140.⁸ For the decarbonylation reaction, the relative rates for breaking the R-C bonds in RCO· (at 135°) for *n*-Pr, *i*-Pr, and *t*-Bu are 1, 8.3, and 90.⁹ For the phenylketene acetals **1**, the relative rate sequence for Me, Et, *sec*-Bu, and *t*-amyl is 1, 1.8, 3.8, and 5.2.

A more apt comparison may be drawn between the relative rates of decomposition of phenylketene acetals and of azo compounds. Decompositions of azo compounds give radicals and nitrogen, and show a low radical-stability effect. The decomposition of azomethane in isooctane has a quantum yield of 0.17.¹⁰ The decomposition of azocumene in benzene has a quantum yield of 0.60.¹¹ These decompositions are known to give radicals, yet the cumyl radical is formed only 3.5 times faster than the relatively unstable methyl radical. Thus the decompositions of azo compounds exhibit sensitivities to the relative stabilities of the radicals produced even lower than those determined for phenylketene acetals. When a strong bond must be broken in a rate-determining step and a large activation energy is required, large rate enhancements are found

(7) (a) G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3037 (1961); (b) G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *ibid.*, 4177 (1960); (c) G. L. Esteban, J. A. Kerr, and A. F. Trotman-Dickenson, *ibid.*, 3873 (1963); (d) W. M. Jackson and J. R. McNesby, *J. Am. Chem. Soc.*, **83**, 4891 (1961); (e) W. E. Falconer, B. S. Rabinovitch, and R. J. Cvetanović, *J. Chem. Phys.*, **39**, 40 (1963); (f) P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964); (g) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953); (h) H. Teranishi and S. W. Benson, *J. Am. Chem. Soc.*, **85**, 2887 (1963); (i) D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963); (j) M. Szwarc, *Chem. Rev.*, **47**, 75 (1950); (k) S. W. Benson, A. N. Bose, and P. Nangia, *J. Am. Chem. Soc.*, **85**, 1388 (1963); (l) D. M. Golden, R. Walsh, and S. W. Benson, *ibid.*, **87**, 4053 (1965); (m) R. Walsh, D. M. Golden, and S. W. Benson, *ibid.*, **88**, 650 (1966).

(8) C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963).

(9) D. E. Applequist and L. Kaplan, *ibid.*, **87**, 2194 (1965).

(10) R. F. Hutton and C. Steel, *ibid.*, **86**, 745 (1964).

(11) S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 137, 143 (1966).

for groups that give rise to a more stable radical. Reactions involving cleavage of weak bonds and requiring lower activation energies show a diminished response of reaction rate to relative stability of radical products. The photoreactions of the azo compounds and phenylketene acetals involve an exothermic decomposition of energy-rich photoexcited states; ground-state species are involved in the hypohalite and aldehyde decompositions. The lower free energy of activation for the decomposition of the photoexcited compounds results in the observed low sensitivities to relative radical stability. The good low-slope, free-energy correlation of Figure 1 is totally consistent with the homolytic cleavage of a R-O bond in a photoexcited phenylketene acetal to give two radicals.

Solvent Effects on Relative Quantum Yields and Product Distributions. The absence of an appreciable solvent effect on the relative quantum yields for photodecomposition of phenylketene acetals upon changing the solvent from cyclohexane to 15% cumene in cyclohexane to 1-methylcyclopentene is evident from the data in Table II. The distribution of products, however, derived from phenylketene diethyl acetal (**1b**) does change with solvent changes (Table III).

Table III. Solvent Effects on Product Distributions from Photolyses of Phenylketene Diethyl Acetal

Compd	Solvent		
	Cyclohexane	15% cumene in cyclohexane	1-Methyl- cyclopentene
4b	31	33	39
5b	59	57	52.5
7b	9	9	8.5
6	1	1	...
5b/4b	1.9 ± 0.13 (4 runs)	1.7 ± 0.1 (2 runs)	1.3 ± 0.1 (2 runs)

One of the products from the photolysis of a phenylketene acetal is the corresponding ester of phenylacetic acid. Reaction of a phenylketene acetal with moisture would give the same ester, and possibly some of the alkyl ester observed is produced thusly, rather than by a photochemical process. Since some of the starting ketene acetal remains at the termination of a reaction, the amount of normal ester obtained after work-up of a reaction mixture will be somewhat higher than the amount actually formed in the photoreaction. Accurate yields of this ester therefore are best obtained by determining its concentration relative to those of the other compounds during the reaction. Product yields in this paper generally refer to those determined by vpc during the course of a reaction. The fact that the concentration of **4b** increased at a steady rate in the solution of **1b** exposed to radiation, while it did not form in a control solution treated identically in all respects except that the ultraviolet radiation was blocked out, establishes it as a photoproduct, not an artifact caused by reaction of the ketene acetal with moisture.

The lack of solvent effect on the relative quantum yields for photodecomposition and the demonstration of a solvent effect on product distributions are both consistent with a mechanism involving homolytic decomposition of a photoexcited state, followed by

reaction of the radical pair produced with one another or with solvent. As radical abstraction of hydrogen from the solvent becomes more likely, the ratio of rearrangement products **5b** and **7b** to reduction product **4b** falls steadily. The yield of ethyl phenylacetate (**4b**) from the diethyl acetal **1b** goes up as the solvent is changed from cyclohexane to 15% cumene in cyclohexane to 1-methylcyclopentene, and the yield of the rearranged ester **5b** goes down. This demonstrates that at least some of the rearranged ester is formed in a nonconcerted process such as the radical-pair formulation given above.

The insensitivity of relative quantum yields to the solvent changes rules out a chain-radical mechanism for the photodecomposition, in agreement with the results from the crossover experiment.

Structural Effects on Product Distributions. In the caged-radical mechanistic formulation, homolysis of a C-O bond in a photoexcited phenylketene acetal molecule produces a pair of radicals which may recombine or react with solvent. The corresponding product ratio of rearranged esters to phenylacetates gives a measure of the efficiency of recombination within the solvent cage, and was shown to depend on the solvent in the expected fashion. This ratio should also be dependent on the relative stability of the alkyl radical within the solvent cage: relatively unstable alkyl radicals should recombine with the carbalkoxybenzyl radical efficiently, while comparatively stable alkyl radicals should afford the carbalkoxybenzyl radicals better opportunity to abstract a hydrogen atom from the solvent. This expectation has been verified experimentally. The relevant data are shown in Table IV.

Table IV. Yields of Esters from Photolyses of Phenylketene Acetals

Acetal 1	R	Yield, ^a %			Product ratio, (5 + 7)/ 4
		Phenyl- acetate 4	alkyl- acetate 5	<i>o</i> -Alkyl- phenyl- acetate 7	
a	Me	5	87	8	19
b	Et	31	59	9	2.2
c	<i>n</i> -Pr ^b	28	55	5	2.1 ^c
d	<i>i</i> -Pr	42	53	5	1.4

^a Determined by vpc analyses during photolyses in cyclohexane at 25°, relative to total esters as 100%. ^b Other products: *n*-propyl *o*-phenylisovalerate, 9%; *n*-propyl *o*-(isopropyl)phenylacetate, 3%. ^c The ratio of total rearranged products (**5c**, **7c**, and the two isopropyl esters) to *n*-propyl phenylacetate is 2.6.

The product ratios (**5** + **7**)/**4** are sensitive to the relative stability of the alkyl radical produced in the homolysis. The dimethyl acetal **1a** gives only 5% of methyl phenylacetate (**5a**), while the diisopropyl acetal **1d** gives 42% of isopropyl phenylacetate (**5d**).

The trend in this work follows closely results reported in the literature. Thus, Lyon and Levy¹² found that methyl radicals formed from the photolysis of azomethane and *d*₆-azomethane in isociane reacted with greater than 99% cage efficiency. Cumyl radicals on the other hand produced photochemically in toluene at 20–40° show a cage efficiency of 35–40%.¹¹ Formation

(12) R. K. Lyon and D. H. Levy, *J. Am. Chem. Soc.*, **83**, 4290 (1961).

of radicals of intermediate stability as in the photodecomposition of 2,2'-azobisisobutyrate in carbon tetrachloride¹³ resulted in a 62% cage efficiency.

Mazur and co-workers¹⁴ have demonstrated that the rearrangement of the acetyl group in steroidal vinyl acetates is essentially internal. The only products formed from the photolysis of mixtures of 5 α -androst-2-ene-3,17 β -diol *d*₅-diacetate and cholest-2-en-3-ol acetate are 2-*d*₃-acetyl-5 α -androstan-3-one-17 β -ol *d*₃-acetate and 2-acetylcholestan-3-one. For other vinyl acetates, particularly those having a fully substituted vinyl group, up to 40% of the products were formed through either internal elimination or noncage-radical processes.

No pattern regarding the relative amounts of 1,3 and 1,5 migrations in the photolysis of the phenylketene acetals is apparent. For phenylketene dimethyl, diethyl, di-*n*-propyl, and diisopropyl acetals, the ratios of the alkyl phenylalkylacetates to the alkyl *o*-alkylphenylacetates ranges between 6 and 11 (Table IV). Since the *o*-alkylphenylacetates are but minor products, the ratios derived from the yield data are subject to large uncertainties.

Gorodetsky and Mazur¹⁵ observed a 1,3 to 1,5 ratio of slightly greater than 4 for the migration of the acetyl group in androsta-3,5-diene-3,17 β -diol diacetate.

Summary and Conclusions

The intramolecular character of the photolytic rearrangement reactions of phenylketene acetals and the insensitivity of relative quantum yields for the photodecomposition of the acetals to the number of easily abstractable hydrogens in the solvent clearly rule out chain-radical or long-lived free-radical processes as important components of the over-all reaction mechanism. The observed variations in product ratios with solvent or structural changes are consistent with production of all of the fragmentation and rearrangement products from a caged-radical pair. In particular, the dramatic change in the ratio of phenylalkylacetate and *o*-alkylphenylacetate to phenylacetate, from 19 to 1.4 on changing from the dimethyl (**1a**) to the diisopropyl acetal (**1d**), is expected for a caged-radical process, but unprecedented in competitive situations involving radical fragmentations and concerted 1,3-sigmatropic cycloreactions.

Experimental Section¹⁶

Crossover Experiment. Solutions containing weighed amounts of methyl α -phenylbutyrate, ethyl α -phenylpropionate, ethyl

(13) G. S. Hammond and J. R. Fox, *J. Am. Chem. Soc.*, **86**, 1918 (1964).

(14) A. Yogev, M. Gorodetsky, and Y. Mazur, *ibid.*, **86**, 5208 (1964).

(15) M. Gorodetsky and Y. Mazur, *ibid.*, **86**, 5213 (1964).

phenylacetate, methyl phenylacetate, and ethyl α -phenylbutyrate in cyclohexane were concentrated at reduced pressure, and the residues were distilled. Mass spectrometric analyses of the distillates at both 15 and 70 eV established a linear relationship between the peak-height ratio *m/e* 192/178 and the mole per cent of ethyl α -phenylbutyrate in the esters of molecular weight 178 or 192, between 0.1 and 4.4 mole %.

Known mixtures of the diethyl acetal **1b** and the phenylketene ethyl methyl acetal (**2a**) used in the crossover experiment were prepared and analyzed by vpc to give a working curve relating area per cent of the vapor phase chromatogram to mole per cent of the diethyl acetal (**1b**). The ethyl methyl acetal (**2a**) used for the crossover experiment was found by the vpc analyses to be contaminated with 4.6 \pm 1% of the diethyl acetal (**1b**).

Photolysis of phenylketene ethyl methyl acetal (**2a**) in cyclohexane gave a product mixture which, after the work-up used for the samples which established the mass spectrometric working curve, was analyzed by mass spectrometry. The peak height ratio *m/e* 192/178 revealed 4.5 \pm 0.5% of ethyl α -phenylbutyrate in the products of molecular weight 178 and 192.

Photolysis Methods. The solvents cyclohexane, cumene, and 1-methylcyclopentene were distilled from potassium or sodium in an inert atmosphere.

The relative quantum yields of the various phenylketene acetals were obtained with solutions of the acetals in 13-mm (o.d.) Vycor test tubes fitted with rubber serum caps, placed 5 cm from the center of a high-pressure 450-w Hanovia mercury lamp equipped with a Vycor filter and a quartz cooling jacket on a rotating turntable in a deionized water bath at 25°. The coarse temperature control of the system was maintained by passing cold tap water through the quartz lamp holder and into a copper coil immersed in the bath. The fine control was effected with a mercury thermostat and knife blade heater. The progress of the reactions was followed by withdrawing 4–15- μ l samples of the solution initially 0.2 to 0.05 *M*, diluting them to 10 ml with dry cyclohexane, and scanning the spectrum of the resulting solution on the ultraviolet spectrometer. When the reactions were followed by vpc, 20–60- μ l samples of the solution (initially 0.2 to 0.5 *M*) were withdrawn and analyzed using the 1.5-m Apiezon L column at 180–185°.

For some compounds studied, a coating formed during the course of the reaction. This was true for 2-benzylidene-*m*-1,3-dioxane (**3a**), 2-benzylidenedioxolane (**3b**), 3-ethoxy-1H-benzopyran (**3c**), and phenylketene divinyl acetal (**1f**). For **3a**, an initial concentration of less than 0.08 *M* minimized the problem. For **3b**, concentrations of less than 0.05 *M* minimized the rate of film formation and permitted some data to be obtained. The benzopyran derivative **3c** started to coat the tube almost from the start even with initial concentrations of less than 0.04 *M*. By taking many ultraviolet samples in the first 2 to 3 hr and by periodically turning the tube to expose a clean side, some data were obtained for this compound. The study of the divinyl acetal **1f** was discontinued after the first preliminary run.

(16) Ultraviolet spectra were recorded with a Perkin-Elmer Model 202 spectrometer, purchased with funds provided by the Research Board of the University of Illinois. Mass spectra were obtained by Mr. J. Wrona on an Atlas CH-4 instrument. Analyses by vpc were accomplished with an Aerograph vapor phase chromatograph Model A-90-P using a Brown recorder equipped with a disk integrator. A 1.5-m Apiezon L (20% on nonacid-washed Chromosorb W) column at 180–190° was used for most of the vpc work.