to be to assume that triplet acetone retains some vibrational excitation when it sensitizes the cyclobutene, although it is assumed that such "hot" molecules come into thermal equilibrium with the surrounding in about 10^{-12} sec. Further experiments to clarify these points are being undertaken.

Experimental Section

Cyclobutene was prepared by the photoisomerization of 1,3-butadiene. The experimental sample was at least 99.4% pure. The only impurity was bicyclo[1.1.0]butane. Butadiene was undetectable in the sample, either before or after the photosensitized reaction. Acetone (Eastman Kodak Spectrograde) was used as obtained.

Irradiations were carried out in cylindrical quartz or Pyrex tubes, 1 cm in diameter. The surface of the tube above the liquid level was covered with black tape to eliminate reactions in the vapor phase. The light source was a bank of 16 low-pressure mercury resonance lamps arranged in a circle around the cell, or 16 fluorescent lamps with their emission peaked at 3130 A arranged similarly.[11] Absorbed intensities were 1.09×10^{18} quanta/ml/min at 2537 A, and 3.24×10^{17} quanta/ml/min at 3130 A. The light sources were calibrated with a uranyl oxalate actinometer.

In quantitative studies, a measured quantity (1 to 4 ml) of acetone was added to the cell, which was then attached to a vacuum line and degassed. The cyclobutene which was stored as a gas sample on the line was measured volumetrically and condensed into the same cell. The cell was sealed and detached from the line. Condensation of a significant quantity of mercury was avoided. At the end of the irradiation the cell was cooled and cut open, and the contents was analyzed by vapor phase chromatography.

Preparation of Cyclobutylacetone. A solution of cyclobutene (100 ml, 0.25 *M*) in acetone was irradiated at 3130 A at an intensity of 10^{18} quanta/ml/min for 36 hr. The solution was worked up by distillation followed by vapor phase chromatography to give 1.2 g of cyclobutylacetone (60%), bp 154°, $n^{24.5}\text{D}$ 1.4328; 2,4-dinitrophenylhydrazone had mp 133.0 (Kofler hot stage (lit.[12] mp 131–133°).

Preparation of I and III. A solution (30 ml, 4 *M*) of cyclobutene in acetone was irradiated in a Rayonet reactor[11] for 24 hr. The reaction was stopped and the unreacted acetone and cyclobutene were recovered by distillation. The residue was separated by vapor phase chromatography (2-m Ucon oil column 100°) into (i) 1.0 g (35%), and (III) 0.25 g (10%).

5-Methyl-4-hexenal 2,4-dinitrophenylhydrazone had mp 133 (lit.[13] mp 133°).

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[11] Supplied by the Southern New England Ultraviolet Co., Middletown, Conn.

[12] A. Burger, R. T. Scandridge, N. E. Stjernstrom, and P. Marchini, *J. Med. Pharm. Chem.*, 4, 517 (1961).

[13] A. Lauchenauer and H. Schinz, *Helv. Chim. Acta*, 32, 1265 (1949).

Photolyses of Phenylketene Acetals

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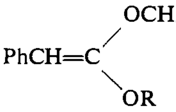
Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received April 21, 1966*

Abstract: Eight phenylketene dialkyl acetals have been photolyzed in cyclohexane and found to give a diversity of products: alkenes, alkylphenylacetates, phenylalkylacetates, phenylcyclohexylacetates, *o*-alkylphenylacetates, and photodimers.

Phenylketene acetals (**1**, **2**, and **3**) offer an attractive subject for photochemical study; their photochemical behavior might be expected to show informative correspondences with three unrelated processes: thermal decompositions of phenylketene acetals, thermal or photolytic decompositions of aryl and vinyl ethers and esters, and photodimerization of styrenes. The photochemistry of eight phenylketene acetals (**1**, **2**, and **3**), prepared by dehydrobromination of the corresponding α-bromophenylacetaldehyde acetals,[2] has been investigated in this initial survey.

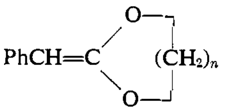
$PhCH{=}C(OR)_2$

1a, R = Me
b, R = Et
c, R = *n*-Pr
d, R = *i*-Pr



$PhCH{=}C(OCH_3)(OR)$

2a, R = Et
b, R = *sec*-Bu



$PhCH{=}C{<}(O)_2(CH_2)_n$

3a, *n* = 3
b, *n* = 2

Results

Identifications of the products obtained through photochemical decompositions of phenylketene acetals were accomplished through spectroscopic methods and comparisons with known compounds. We first summarize the products derived photolytically from **1**, **2**, and **3** and control experiments demonstrating that they are primary photoproducts, then describe syntheses of needed reference compounds.

Photoproducts from Phenylketene Acetals. The structures of the major photoproducts from photolyses of phenylketene acetals in cyclohexane were demonstrated principally by their nmr spectra. The other spectral and physical properties determined for these compounds were in agreement with the assigned structures. Structures of the minor products were assigned mainly from their vpc retention times and infrared spectral comparisons with authentic materials. Certain nmr peaks attributable to some of the minor products could be seen and assigned in spectra obtained for the photomixture or for enriched distillation fractions.

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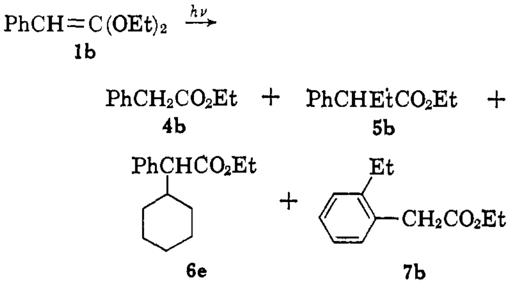
[1] National Science Foundation Cooperative Graduate Fellow, 1963–1966.

[2] J. E. Baldwin and L. E. Walker, to be published.

The principal products from the photolysis of phenylketene diethyl acetal (**1b**) were found to be ethyl phenylacetate (**4b**) and ethyl α-phenylbutyrate (**5b**). Together **4b** and **5b** amounted to about 90% of the volatile products. Some 3–5% of ethylene was trapped in a chloroform solution of bromine and identified as the dibromide. Minor products detected and isolated by vpc proved to be ethyl phenylcyclohexylacetate (**6e**) and ethyl *o*-ethylphenylacetate (**7**).



Ethyl phenylacetate and ethyl α-phenylbutyrate were identified by their clear-cut nmr spectra. Infrared and mass spectra (parent peaks at *m/e* 164 and 192) were also in agreement with the assigned structures. The benzylamide derivative from **5b** had mp 86–88°. A literature value[3] for this compound is 77–78°. However, the same derivative prepared from authentic **5b** gave mp 87–89°. Ethylene dibromide was identified through its characteristic nmr spectrum (singlet at τ 6.4) and refractive index.

Ethyl phenylcyclohexylacetate (**6e**) and ethyl *o*-ethylphenylacetate (**7b**) were suggested from the retention times of two small peaks in the vapor phase chromatogram of the product mixture. Retention times for these two compounds were identical with those of authentic materials. The structures of these esters were confirmed through direct comparisons with infrared, or infrared and nmr spectra of authentic samples.

A small yield of a dimer of phenylketene diethyl acetal was obtained through chromatographing the crude photomixture. On one occasion, it crystallized from the cooled photomixture. The molecular formula $C_{24}H_{32}O_4$ was established for this solid of mp 152–154°, $\lambda_{\max}^{\mathrm{EtOH}}$ 220 mμ (ϵ 3100), 254 (450), 259 (640), and 265 (510). Its nmr spectrum showed a multiplet at τ 2.6–2.9 (10 H), a singlet at 6.3 (2 H), and the characteristic ethyl patterns centered at 6.75 (8 H) and 8.95 (12 H). Whether the photodimer should be formulated as a head-to-head or a head-to-tail cycloadduct, and the stereochemistry of the dimer have not been investigated. Hydrolysis of this dimer to 2,4-diphenylcyclobutane-1,3-dione[4,5] or hydrolysis and dehydrogenation to 3,4-diphenylcyclobut-3-ene-1,2-dione[6] should provide an answer to the structural problem.

Photolyses of phenylketene dimethyl acetal (**1a**), di-*n*-propyl acetal (**1c**), and diisopropyl acetal (**1d**) similarly gave the esters **4a,c,d** and **5a,c,d**, corresponding to the major products derived from the diethyl acetal. For the methyl and *n*-propyl cases, the esters **4a** and **5a**, **4c**, and **5c** were separated by column chromatography and identified by their nmr spectra. The rearranged methyl ester (**5a**) was hydrolyzed to the acid followed by conversion to the amide. The latter had a melting point of 91–92° compared to a literature value[7] of 92°. The major products (**4d** and **5d**) from the diisopropyl acetal were isolated by vpc and identified by comparisons of their infrared spectra with those of authentic materials. Peaks ascribed to these esters were observed in the nmr spectrum of the product mixture. Some 1,2-dibromopropane was obtained from a bromine trap after irradiation of **1c**.

Alkyl *o*-alkylphenylacetates (**7**) were evident in the vapor-phase chromatograms of the product mixtures. Mixtures of *n*-propyl *o*- and *p*-(*n*-propyl)- and isopropyl *o*- and *p*-(isopropyl)phenylacetates were prepared for comparison with the photomixtures from **1c** and **1d**. In each case, a peak in the product mixture corresponded to the *ortho* ester but none to the *para* isomer. The aromatic hydrogens of the ring-substituted esters are observed in the nmr spectrum of the photoproduct mixtures.

One unanticipated product was uncovered in the reaction mixture from the photolysis of phenylketene di-*n*-propyl acetal (**1c**) and positively identified as *n*-propyl α-phenylisovalerate (**6g**). The infrared spectra of this photoproduct and that of an authentic sample of *n*-propyl α-phenylisovalerate were identical. In addition the benzylic proton in **6g** (doublet at τ 6.9 with $J \sim 10$ cps) could be seen in the nmr spectrum of certain mixtures of the major photoproducts. Another minor product from this reaction had the same vpc retention time as authentic *n*-propyl *o*-(isopropyl)-phenylacetate but was not conclusively identified.

These minor products from phenylketene di-*n*-propyl acetal containing the isopropyl group were shown to not be photochemically produced from *n*-propyl phenylacetate (**4c**) or *n*-propyl α-phenylvalerate (**5c**). No peaks attributable to the known phenylketene diisopropyl acetal or to the unknown phenylketene *n*-propyl isopropyl acetal were observed in the vapor phase chromatogram of the starting phenylketene di-*n*-propyl acetal, thus ruling out the possibility of the formation of **6g** from starting material containing an isopropyl group. Phenylketene *n*-propyl isopropyl acetal would be expected to fall between the diisopropyl and di-*n*-propyl acetals on vapor phase chromatograms, and, if it were present in the starting material, it should have been seen by vpc analysis.

Twice as many photoproducts from the mixed acetals **2** as from the acetals **1** were expected and the resultant complexity in the product mixture was observed. Photolysis of phenylketene ethyl methyl acetal (**2a**) gave ethyl α-phenylpropionate (**6a**), methyl α-phenylbutyrate (**6c**), ethyl phenylacetate (**4b**), methyl phenylacetate (**4a**), and traces of both ethyl and methyl phenylcyclohexylacetates. Both the nmr spectrum and the vapor phase chromatogram of the distilled product mixture suggested low yields of the isomers of **7**. The *sec*-butyl methyl acetal **2b** similarly gave the four anticipated major products **4a**, **4e**, **6b**, and **6d**.

The two cyclic phenylketene acetals **3** gave quite different photolysis products. 2-Benzylidene *m*-1,3-

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[3] G. S. Skinner and J. F. Perkins, Jr., *J. Am. Chem. Soc.*, **72**, 5569 (1950).

[4] J. E. Baldwin and J. D. Roberts, *ibid.*, **85**, 2444 (1963).

[5] D. G. Farnum, J. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, *ibid.*, **87**, 5191 (1965).

[6] A. T. Blomquist and E. A. LaLancette, *ibid.*, **83**, 1387 (1961).

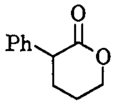
[7] I. Heilbron, "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965.

Table I. Yields and Properties of Some Phenylalkylacetic Acids

Alkyl group	Method	Bp, °C	Pressure, mm	n^{20}D or mp, °C	Yield	Literature values			
						Ref	Bp, °C	Pressure, mm	n^{24}D or mp, °C
Et	*a*	102–104	0.4	41–43	88	*b*	145–150	14	44–45
Me	*c*	105–110	0.5	1.5229	63	*c,d*	145–147	12	1.5250
n-Pr	*e*	99–112	0.4	1.5118[f]	20[g]	*h*	132	3	51–52
i-Pr	*e*	107–115	0.5	61–62[i]	26[g]	*j*			61–63
sec-Bu	*e*	115–118	0.2	1.5113[f,k]	31[g]				
Cyclohexyl	*e*			147–149[l]	12[g]	*b*			147–148

[a] See ref 12, p 150. [b] See ref 7. [c] See ref 11. [d] See ref 17. [e] See ref 8. [f] Solidified on standing. [g] Based on phenylacetonitrile. [h] C. G. Overberger and D. Tanner, *J. Am. Chem. Soc.*, **77**, 369 (1955). [i] From pentane. [j] D. J. Cram, H. L. Nyquist, and F. A. A. Elhafez, *J. Am. Chem. Soc.*, **79**, 2876 (1957). [k] Amide mp 101–103°, recrystallized from ethanol–water. [l] From ethanol–water.

dioxane (**3a**) gave the δ-lactone **8**, isolated in 40% crude yield by distillation, as the only identifiable product. It was further purified by column chromatography. Spectral data and elemental analysis confirmed the structural assignment.



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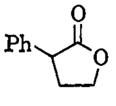

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2-Benzylidenedioxolane (**3b**) did not give an isolable yield of the expected lactone **9**; instead a photodimer was obtained. This dimer, $C_{20}H_{20}O_4$, mp 213–215°, $\lambda_{\max}^{\mathrm{EtOH}}$ 226 mμ (ε 9500), 253 (500), and 258 (530), had nmr absorptions at τ 2.3–2.8 (10 H), a singlet at 5.9 (2 H), and a singlet at 6.4 (8 H). Like the dimer from phenylketene diethyl acetal, its structure presumably could be readily determined through degradation.

Control Experiments. One of the products from the photolysis of a phenylketene acetal is the corresponding ester of phenylacetic acid. Since the phenylketene acetal would react with moisture to give the same ester, some or all of the ester could conceivably be produced through reaction of the starting material with adventitious water. But analyses of photolysis mixtures at various time intervals by vpc show the phenylacetates to be genuine photoproducts; similar analyses with identical solutions of a phenylketene acetal in cyclohexane protected from light do not show systematic increases in the concentration of a phenylacetate.

The two major products from phenylketene diethyl acetal (**4b** and **5b**) were irradiated under the conditions of a normal photoreaction to determine if any of the minor products might come from further decomposition of these esters, rather than directly from the diethyl acetal. Compounds **4b** and **5b** decompose when irradiated in cyclohexane but neither gives any of the minor products. New peaks in the vapor phase chromatogram of the concentrated mixture from this irradiation have not been assigned but all have retention times different from those of **6e** and **7b**. The ester products appear to be unaffected until the high-absorbing phenylketene acetal has largely disappeared. Indeed, concentration *vs.* time plots for the formation of **4b** and **5b**, linear for 80% conversion of **1b**, begin to curve toward a lower rate of formation of these esters beyond 80% conversion and even level off to a steady-state region.

Ethyl orthophenylacetate, a possible impurity in **1b** due to its reaction with moisture, was also subjected to the photolysis conditions. This ortho ester is photochemically more stable than the esters. No peaks ascribed to the minor products were observed on vapor phase chromatograms of the product mixture from the photolysis of this orthoester.

Syntheses of Phenylacetates and Phenylalkylacetates. Most of the esters derived from the photolyses of phenylketene acetals are easily obtained by other methods, and have been prepared for spectral and vpc comparisons with the photoproducts.

Phenylalkylacetic acids were usually prepared following the three-step procedure of Pattersson and Willdeck.[8] This method was preferred for the required small-scale preparations over a two-step method involving first alkylation with sodium amide in liquid ammonia followed by hydrolysis.[9] Hauser and coworkers[10] have prepared similar acids by alkylations of phenylacetic esters with halides by means of either sodium amide in liquid ammonia or sodium hydride followed by hydrolysis. α-Phenylpropionic acid was prepared by oxidation of hydrotropaldehyde with silver oxide.[11] The properties of the acids obtained in this work and literature values are given in Table I.

The required esters of phenylacetic acid were obtained by hydrolysis of phenylketene acetals, alcoholysis of phenylacetyl chloride,[12] or reaction of phenylacetonitrile with an alcohol and sulfuric acid.[13] The phenylalkylacetates were prepared from the acids by way of the acid chlorides.

A mixture of ethyl *o*- and *p*-ethylphenylacetates was prepared by chloromethylation of ethylbenzene[14] followed by treatment with sodium cyanide[15] and then with ethanol and sulfuric acid.[13] This route was adapted to prepare mixtures of *n*-propyl *o*- and *p*-(*n*-propyl)-, *n*-propyl *o*- and *p*-(isopropyl)-, and isopropyl *o*- and *p*-(isopropyl)phenylacetates. With primary alkyl groups on the benzene ring the method gave 20–25% of the *ortho* isomer and 75–80% of the *para* isomer. For the secondary alkyl benzene, the *ortho*:*para* ratio was 13:87. The structural assignment for the isomers of the ethyl compounds was based both on

(8) K. Pattersson and G. Willdeck, *Arkiv Kemi.*, **9**, 333 (1956).

(9) E. M. Hancock and A. C. Cope, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 219.

(10) (a) W. G. Kenyon, R. B. Meyer, and C. R. Hauser, *J. Org. Chem.*, **28**, 3108 (1963); (b) W. G. Kenyon, E. M. Kaiser, and C. R. Hauser, *ibid.*, **30**, 2937 (1965).

(11) E. L. Eliel and J. P. Freeman, *J. Am. Chem. Soc.*, **74**, 923 (1952).

(12) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 200.

(13) R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p 270.

(14) G. S. Skinner, J. A. Gladner, and R. F. Heitmiller, *J. Am. Chem. Soc.*, 73, 2230 (1951).

(15) See ref 13, p 107.

Table II. Properties of Phenylalkylacetates and Related Esters

Structure		R or R/R′	Bp, °C	Pressure, mm	$n^{20}D$	Literature values Bp, °C	Literature values Pressure, mm	Literature values Ref
$PhCH_2CO_2R$ (**4**)	a	Me	45–50	0.2	1.5081	57–60	0.5	*e*
	b	Et	46–48	0.4	1.4975	120–125	17–18	*f*
	c	*n*-Pr	67–70	0.3	1.4900	238		*f*
	d	*i*-Pr			1.4950			
	e	*sec*-Bu	56–57	0.3	1.4872	100	2	*g*
$PhCHRCO_2R$ (**5**)	a	Me	41	0.15	1.5019	98–100	12	*e*
	b	Et[a]	54–58	0.4	1.4895	149	47.5	*h*
	c	*n*-Pr	83–84	0.4	1.4858			
	d	*i*-Pr	53–55	0.1	1.4948			
$PhCHRCO_2R'$ (**6**)	a	Me/Et[b]	51–52	0.2	1.4920			
	b	Me/*sec*-Bu	72	0.5	1.4824			
	c	Et/Me[c]	52	0.2	1.4963	115–118	19	*i*
	d	*sec*-Bu/Me[d]	71–72	0.4	1.4946	125–127	12	*j*
	e	Cyclohexyl/Et	107–110	0.3	1.5110	130	1.6	*k*
	f	Cyclohexyl/Me	108	0.4	1.5171			
	g	i-Pr/*n*-Pr	74–85	0.2	1.4842			

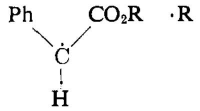
[a] For ester from the photolysis of **lb**. *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.34. Found: C, 75.00; H, 8.59. [b] *Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.93; H, 7.88. [c] *Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.31; H, 7.97. [d] *Anal.* Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.80; H, 8.59. [e] See ref 17. [f] See ref 7. [g] A. B. H. Funcke, M. J. E. Ernsting, J. Gootjes, R. F. Rekker, and W. Th. Nauta, *Arzneimittel-Forsch.*, **4**, 492 (1954); *Cf. Chem. Abstr.*, **49**, 10888*c* (1955). [h] K. C. Bachman, A. Zimmerli, and E. L. Simons, *Ind. Eng. Chem.*, **42**, 2569 (1950). [i] See ref 10a. [j] H. Martin and E. Habicht, German Patent 1,038,548 (1958); *cf. Chem. Abstr.*, **54**, P18444*b* (1960). [k] J. O. Jílek and M. Protiva, *Czech. Farm.*, **6**, 113 (1957); *cf. Chem. Abstr.*, **51**, 14596*b* (1957).

infrared spectra and literature data. The minor isomer showed a band at 750 cm^{-1} characteristic of *ortho* substitution.[16] The major isomer absorbed at 820 cm^{-1}, a band assignable to the *para* isomer.[16] Furthermore, Skinner and co-workers[14] have separated the intermediate nitriles *via* the crystalline ethyl alkyl-β-cyano-α-hydroxycinnamates and have found the *para* isomer to be the predominant one.

The phenylacetates and phenylalkylacetates prepared in the course of this work, and their physical properties, are summarized in Table II. Each ester had infrared and nmr spectra consistent with the assigned structure and in agreement with earlier reports.[10b] Further conformation of the structural assignments through elemental analysis, infrared spectroscopy, and mass spectrometry was secured in some cases. The observed physical properties of the esters compare favorably with published data. However, earlier workers almost invariably used higher pressures for the distillation of their esters so that only qualitative comparisons of boiling points may be made.

Discussion

The spectrum of products obtained upon photolysis of phenylketene acetals delimits the mechanistic possibilities that must be considered, but does not permit a conclusive choice in favor of one of these possibilities. Formation of alkyl phenylcyclohexylacetates is persuasively suggestive of a radical process; homolytic cleavage of a C–O bond in a photoexcited state of the phenylketene acetal could give a pair of radicals (**10**), the alkyl radical of the pair could abstract a proton from cyclohexane, and recombination of the cyclohexyl and carboalkoxybenzyl radicals would produce the observed product. The other rearrangement and decomposition products could similarly be rationalized as resulting from the radical pair **10**, through recombination, disproportionation, or hydrogen abstraction from solvent. Cycloaddition of the photoexcited phenylketene acetal with an unactivated acetal could be competitive with its homolysis and would account for the observed photodimers of **1b** and **3b**.



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This representation of the mechanism of the photoreactions may be compared with published reports on thermolytic decompositions of ketene acetals. Thermal decomposition of phenylketene dimethyl acetal gives methyl α-phenylpropionate, methane, and the *meso* dimer of the carbomethoxybenzyl radical,[17] products indicative of a free-radical mechanism. Thermal rearrangement of ketene diethyl acetal in the presence of *t*-butyl peroxide[18] lends credence to the suggestion that methyl α-phenylpropionate is formed in a chain radical process.

The thermal rearrangement of α-alkoxystyrenes to alkyl phenyl ketones,[19] a transformation formally analogous to the rearrangement **1** → **5**, has been found to be an intermolecular radical reaction.[20] More recently Wiberg and co-workers presented results demonstrating a chain radical mechanism for this reaction.[21]

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(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

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

(18) E. S. Huyser, R. M. Kellogg, and D. T. Wang, *J. Org. Chem.*, 30, 4377 (1965).

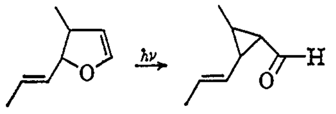
(19) (a) L. Claisen, *Chem. Ber.*, **29**, 2931 (1896); (b) L. Claisen and E. Haase, *ibid.*, **33**, 3778 (1900).

(20) (a) F. H. MacDougall, W. M. Lauer, and M. A. Spielman, *J. Am. Chem. Soc.*, **55**, 4089 (1933); (b) W. M. Lauer and M. A. Spielman, *ibid.*, **55**, 4923 (1933); (c) M. A. Spielman and C. W. Mortenson, *ibid.*, **61**, 666 (1939); (d) C. W. Mortenson and M. A. Spielman, *ibid.*, **62**, 1609 (1940).

(21) (a) K. B. Wiberg and B. I. Rowland, *ibid.*, **77**, 1159 (1955); (b) K. B. Wiberg, T. M. Shryne, and R. R. Kintner, *ibid.*, **79**, 3160 (1957); (c) K. B. Wiberg, R. R. Kintner, and E. L. Motell, *ibid.*, **85**, 450 (1963).

These thermal reactions, however, do not necessarily afford pertinent mechanistic analogies for the corresponding photochemical rearrangement and fragmentation reactions of phenylketene acetals. The thermal 1,3-sigmatropic shift involved in the rearrangements of α-alkoxystyrenes or of **1** $\rightarrow$ **5** would be expected to go in a nonconcerted fashion thermally,[22] and be permitted to go concertedly under photolytic reaction conditions.[22] Whether or not this cycloreaction would in fact be concerted depends on relative rates for possible concerted and nonconcerted pathways, a point not decided by molecular orbital theory and the Woodward–Hoffmann postulates. Thus, the indications of radical intermediates in the thermal decompositions of vinyl ethers and ketene acetals are in agreement with theory, but the photolytic rearrangements of such compounds may be either concerted or nonconcerted.

Little mechanistically conclusive evidence on the photochemistry of vinyl and aryl ethers and esters is available, but they do give products similar to those derived from phenylketene acetals. On irradiation in the gas phase, ethyl vinyl ether yields acetaldehyde, ethylene, and butane.[23] The dihydrofuran derivative **11**[24] gives a mixture of two isomers of **12**. Vinyl benzoates[25] give rearrangement products, through 1,3-acyl migrations. Most vinyl acetates give predominantly rearrangements but some give fragmentation products.[26] Vinyl lactones,[27] however, may decompose photolytically to carbon monoxide, carbon dioxide, ketene, and other products.



11 **12**

The photolysis of phenyl esters, the photo-Fries rearrangement, has been explored for many compounds.[28] The photolytic decompositions of three aromatic ethers, allyl phenyl, diphenyl, and benzyl phenyl ethers, have been briefly investigated. The anticipated ring-alkylated phenols are formed when these ethers and esters are photolyzed.[29] Hence there is a common pattern of reaction products from photolyses of vinyl and aryl ethers and esters and of phenylketene acetals. Whether there exists a common mechanistic pattern beneath both sets of photochemical conversions remains to be seen.

The photodimerization of the phenylketene acetals **1b** and **3b** has ample precedent.[30] It is curious to note that the ethylenedioxy function appears to enhance the reactivity for photochemical cycloadditions of the acetal **3b**, relative to that of **3a**, just as it confers special reactivity for thermal Diels–Alder cycloadditions in ketals of cyclopentadienone.[31] Most of the phenylketene acetals studied in this work did not give appreciable yields of photodimers.

A few specific clues to the mechanism of the photochemical decompositions of phenylketene acetals are indicated by the observed products. Since the cyclic acetal **3a** gives the lactone **9**, the other rearrangement reactions may be predominantly or exclusively intramolecular. A quantitative estimation of the extent of intramolecular or intermolecular rearrangement would of course require quantitative data.

Photolysis of phenylketene di-*n*-propyl acetal (**1c**) gave two products having an isopropyl group in place of an *n*-propyl moiety: *n*-propyl α-phenylisovalerate (**6g**) and *n*-propyl *o*-(isopropyl)phenylacetate. Either the migrating propyl group may rearrange to an isopropyl group between the time it leaves oxygen and participates in formation of a new C–C bond, or an unusual concerted mechanism may account for alkyl migration with rearrangement.

The first group of alternatives would postulate intermediate formation of an *n*-propyl radical and rearrangement of the *n*-propyl to an isopropyl radical prior to recombination with an carboxy-*n*-propylbenzyl radical; or heterolytic C–O bond cleavage with rearrangement from the *n*-propyl to isopropyl cation preceding geminate ion-pair recombination; or homolytic C–O bond cleavage, a one-electron transfer to give an ion pair, rearrangement in the alkyl group, and recombination.

Rearrangement of a *n*-propyl radical to an isopropyl radical appears unprecedented. Some radical rearrangements involving the 1,3 and 1,5 migration of hydrogen atoms have been demonstrated.[32] Olefinic products arising from the reaction of 1-chloro-3-phenylpropene with a Grignard reagent in the presence of cobalt chloride[33] suggest a radical mechanism with either 1,3 or 1,2 migration of a hydrogen atom. Kolbe electrolysis, a process generally thought to go by way of a radical mechanism, converted perhydrodiphenic acids to a γ-lactone rather than to the expected δ-lactone.[34] A mechanism involving the 1,2 migration of a hydrogen in the intermediate diradical has been suggested[34] although other mechanisms may be possible.[32b] Several reactions believed to involve either trimethylene or substituted trimethylene diradicals yield products that formally arise from a 1,2 hydrogen migration in the diradicals. Thus propylene is formed during the thermal interconversion of *cis*- and *trans*-dideuteriocyclopropanes.[35] The photochemical decomposition of cyclobutanone also yields propylene as well as cyclopropane.[36] But no conclusive evidence demonstrating 1,2-hydrogen shifts in monoradical alkyl groups is available.

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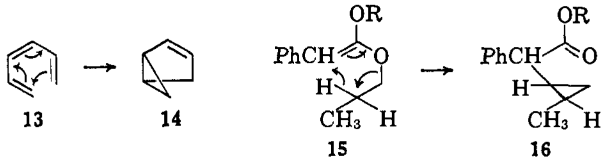
One concerted mechanism that would account for the formation of ester **6g** from the di-*n*-propyl acetal **1c** (**15** → **16**) bears a formal similarity with the known photochemical conversion of 1,3,5-hexatrienes (**13**) to bicyclo[3.1.0]hex-2-enes (**14**).[37] Whether or not this or some other concerted mechanism is operative is not at all sure; it is raised as a possibility to stress our reluctance to conclude, on the basis of products containing a rearranged alkyl group alone, that the rearrangement is nonconcerted.



A priori, more than one mechanism may be operative for the formation of the various products obtained through photolyses of phenylketene acetals. While all of the rearrangement and fragmentation products might arise from the radical pair **10**, some might be formed through concerted cycloreactions. The 1,3- and 1,5-sigmatropic rearrangements **1** → **5** and **1** → **7** might be concerted, although the **1** → **7** reaction would require an antarafacial stereochemistry. The fragmentation reaction **1** → **4** + olefin may not be concerted photochemically,[38] and must involve formation of intermediate fragments.

Thus the principal mechanistic points raised by the photolyses of phenylketene acetals concern the nature of the radicals involved in the production of such products as **4** and **6e**, and the concerted or nonconcerted formation of the major rearranged ester **5**. Are the radicals **10** efficiently caged by solvent, free to react intermolecularly with other molecules or radicals, or able to propagate radical chains? Do they provide the low-energy path for formation of **5**, or can concerted cyclorearrangement of a photoactivated phenylketene acetal to give **5** compete effectively with homolytic decomposition?

These questions have been partially answered through a series of quantitative experiments which will be reported in the near future.[39]

Experimental Section[40]

Phenylalkylacetic acids, needed for preparations of the corresponding esters, were prepared by standard methods. The physical properties, yields, literature citations, and reported values for the physical properties of these six acids are given in Table I.

Esters of phenylacetic acid (4) were prepared by three methods: reaction of a phenylketene acetal with water, addition of an alcohol to phenylacetyl chloride, or treatment of phenylacetonitrile with an alcohol and sulfuric acid. An authentic sample of the isopropyl ester was obtained from the ketene acetal; the *sec*-butyl ester was prepared from the acid chloride; methyl and *n*-propyl esters were available. The observed properties of these esters and literature values are given in Table II.

Esters of phenylalkylacetic acids (5) were prepared treating the corresponding acid chlorides with excess alcohol; following a normal work-up, the esters were purified by distillation. The esters so obtained were at least 90% pure as judged by vpc criteria; their properties are summarized in Table II. Further purification when necessary was achieved by preparative vpc using a 1.5-m Apiezon L column.

Alkyl *o*- and *p*-Alkylphenylacetates. The chloromethylation of ethylbenzene on an 0.4-mole scale (based on ethylbenzene) was carried out following the procedure of Skinner and co-workers[14] to give a 25% yield of the monochloromethylated fraction with bp 87–95° (0.6 mm), n^{20}D 1.5264. The mixture of the isomeric chloromethylethylbenzenes was converted to the isomeric nitriles, bp 117–123° (5 mm), and then to the isomeric esters, bp 81–85° (0.5 mm), n^{20}D 1.4968, by standard procedures.[13,15] Vapor phase chromatographic analysis showed the ester mixture to contain 21% *o*- and 79% *p*-ethylphenylacetates. Some of this mixture was separated into the pure components by preparative vpc.

Using the same procedures, *n*-propylbenzene (0.1 mole) was subjected to the same reactions. The monochloromethyl fraction (24%) had bp 51–73° (0.25 mm). The nitrile mixture was prepared in 73% yield and had bp 82–86° (0.3 mm). The ester mixture had bp 91–95° (0.4 mm), n^{20}D 1.4888. Analysis by vpc indicated a 22:78 mixture of *n*-propyl *o*- and *p*-(*n*-propyl)phenylacetates.

Cumene gave a 42% yield of a monochloromethyl fraction of bp 56–65° (0.2 mm) (lit.[14] bp 116–120° (19 mm)). The nitrile mixture (87%) had bp 86–91° (0.2 mm) (lit.[14] bp 134–137° (14.5 mm)). Treatment of the nitrile mixture with 95% *n*-propyl alcohol and concentrated sulfuric acid in the normal fashion[13,15] gave after work-up a 77% yield of the *n*-propyl *o*- and *p*-(isopropyl)phenylacetates boiling at 84–91° (0.2 mm), n^{20}D 1.4882. Analysis by vpc indicated that the mixture contained *ortho* and *para* isomers in a 13:87 ratio. Some of this ester mixture was hydrolyzed to the acid with 25% sodium hydroxide solution, converted to the acid chloride with thionyl chloride, and treated with isopropyl alcohol to give a mixture of the isopropyl *o*- and *p*-(isopropyl)phenylacetates, bp 85–90° (0.3 mm) (74% yield).

Photolyses of phenylketene acetals[2] were carried out using a high-pressure 450-w Hanovia mercury lamp equipped with a Vycor filter and a quartz cooling jacket. A 350-ml reaction vessel equipped with a gas inlet and joints for a condenser and the quartz lamp assembly were used. Sodium-dried reagent cyclohexane was the solvent. Solutions were stirred both magnetically and by passing through a gentle stream of purified dry nitrogen. The progress of the reactions was followed by ultraviolet spectroscopy.

In some cases, the nitrogen stream leaving the reaction mixture was passed into a solution of bromine in chloroform to trap volatile olefins formed.

After photolysis, a reaction solution was concentrated at reduced pressure to give a crude mixture representing about 90% of the weight of the starting material. Distillation of this crude mixture using a short-path distillation apparatus gave, at best, fractions totaling 90% of the weight of material taken for distillation, boiling point up to 100° (0.2 mm).

The yellow-orange distillation residues which did not boil at 200° (0.2 mm) were not identified. The formation of these residues was minimized by avoiding overexposure of the photolysis solutions to ultraviolet radiation; photolyses were normally stopped after 80–90% of the starting material had disappeared.

The distillate was examined by vpc and by nmr spectroscopy. The major components were isolated by column chromatography on activated silica gel with benzene and benzene–chloroform as eluent. Minor components were collected by vpc.

The photodimer from phenylketene diethyl acetal was isolated by chromatographing the crude photomixture on silica gel and eluting with a 2:1 mixture of toluene–cyclohexane. The crude dimer was eluted before any of the esters in the mixture. The impure dimer was recrystallized from ethanol–water and had mp 152–154°. On one occasion, the crude photomixture on standing in the refrigerator deposited some crystals melting at 155–157°. The nmr and ultraviolet spectral data for this compound are given above.

Anal. Calcd for $C_{24}H_{32}O_4$: C, 75.00; H, 8.34; mol wt, 384.

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[37] W. G. Dauben, 19th National Symposium on Organic Chemistry, Tempe, Ariz., June 14–17, 1965.

[38] J. E. Baldwin, unpublished; R. Hoffmann and R. B. Woodward, unpublished.

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[40] Infrared and nmr spectra were obtained on Perkin-Elmer Models 21 and 521 infrared spectrometers and on a Varian A-60 nmr spectrometer by Mr. O. Norton and associates. Carbon tetrachloride was used as the solvent for nmr spectra. Mass spectra were obtained by Mr. J. Wrona on an Atlas CH-4 instrument. Ultraviolet spectra were recorded with a Perkin-Elmer Model 202 ultraviolet-visible spectrometer, purchased with funds from the Research Board of the University of Illinois. Microanalyses and osmetric molecular weight determinations were carried out by Mr. J. Nemeth and assistants. Analyses by vpc were completed on an Aerograph vapor phase chromatograph Model A-90-P with 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. All boiling and melting points are uncorrected.

Found: C, 74.93; H, 8.28; mol wt (osmometrically in benzene), 388.

The photolysis of 2-benzylidenedioxolane in the normal fashion resulted in the formation of a white insoluable solid. The solid (22% yield) was purified by vacuum sublimation and found to melt at 213–215°.

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21; mol wt, 324. Found: C, 74.19; H, 6.29; mol wt (osmometrically in acetone), 329.

The liquid residue from the photolysis of 2-benzylidenedioxolane was distilled to give some starting material and unidentified liquids having no nmr signals above τ 7.2. From the distillation residue another 21% of crude solid melting over a wide range was obtained.

The crude lactone from 2-benzylidene-*m*-1,3-dioxane was isolated by distillation and had bp 132–138° (0.4 mm). The crude material was chromatographed on silica gel and eluted with 1:1 benzene–chloroform. The liquid was flash distilled to give pure compound having $n^{20}\mathrm{D}$ 1.5511.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.00; H, 6.86. Found: C, 74.30, 74.99; H, 6.80, 7.07.

The Secondary β-Deuterium Isotope Effect and the Cage Effect in the Thermal Decomposition of Azobis-α-phenylethane[1]

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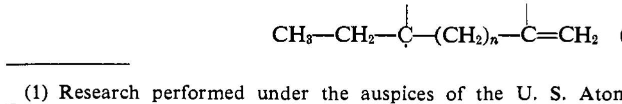
Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973. *Received April 5, 1966*

Abstract: Azobis-α-phenylethane-β,β,β-d_3 was prepared and its rate of decomposition in ethylbenzene at 105° was compared to that for the natural compound. Calculations indicate that approximately one-fourth of the rate retardation is due to the effect of increased mass on the ratio of imaginary frequencies. The residual β effect in the formation of the α-phenylethyl radical is about one-fourth as large as the comparable β effect in the formation of the α-phenylethyl carbonium ion and suggests that hyperconjugative stabilization in the radical is somewhat diminished in comparison with the ion. In addition the cage effect was measured in the absence of scavengers.

The stabilization of carbonium ions by delocalization of charge on neighboring β-hydrogen atoms is well known and has received considerable attention.[2] Hyperconjugation in radical transition states or intermediates has not been as well established. The best evidence arises from electron spin resonance spectra.[3] Contributions of hyperconjugative resonance forms to the electronic structure, for example, of the ethyl radical allows an explanation for the approximately 5% of free spin density in each of the methyl hydrogen 1s orbitals.[4]

Support for hyperconjugation in radicals from kinetic studies is weaker and less obvious. In a study of the polymerization of *p*-alkyl-substituted styrenes initiated by azobisisobutyronitrile, the relative rates were found to follow the Baker–Nathan order, methyl > ethyl > *t*-butyl.[5] The ratio of rates between the fastest and slowest, however, was only a factor of 1.2. The addition of methyl radicals to isolated dienes also exhibits a small rate enhancement when R is changed from H to CH_3 (eq 1).[6] For example, the rate of methyl addition to 2,4-dimethylhexadiene-1,5 is 10–15% faster than to the unsubstituted hexadiene. Similarly, addition to 2,3-dimethylbutadiene is about 7% more rapid than to butadiene itself. This increase in rate has been attributed to hyperconjugative stabilization of the radical-like transition state.[6] A possible reason for the very small enhancement may be the resemblance of the transition state to the reactant state rather than to the product radical.[7]



$$\mathrm{CH_3\cdot + CH_2{=}\overset{R}{C}{-}(CH_2)_n{-}\overset{R}{C}{=}CH_2 \longrightarrow CH_3{-}CH_2{-}\overset{R}{\underset{\cdot}{C}}{-}(CH_2)_n{-}\overset{R}{C}{=}CH_2} \qquad (1)$$

One way to investigate the degree of involvement of hyperconjugative stabilization is the study of secondary β-deuterium isotope effects. This tool has already been used extensively by Shiner[8a] and Lewis[8b] in studies of carbonium ion formation although Robertson[8c] has suggested a different mechanism for secondary β-deuterium effects.[8d]

As the first part of an investigation of hyperconjugative stabilization of radicals we describe here the study of the secondary β effect in the thermal decomposition of azobis-α-phenylethane. Since we also have at hand the hexadeuterio azo compound, we have measured the cage effect in the absence of scavengers in ethylbenzene solution.

Experimental Section

Aceto-d_3-phenone Azine. To a solution of 5.34 g (0.0434 mole) of aceto-d_3-phenone[9] in 8 ml of absolute ethanol-d[10] was added 1.63 g

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

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[4] D. B. Chesnut, *J. Chem. Phys.*, **29**, 43 (1958); A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

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[7] M. Field, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 4451 (1962).

[8] (a) V. J. Shiner, *Tetrahedron*, **5**, 243 (1959); (b) E. S. Lewis, R. R. Johnson, and G. M. Coppinger, *J. Am. Chem. Soc.*, **81**, 3140 (1959); (c) K. T. Leffek, R. E. Robertson, and S. E. Sugamori, *Chem. Ind.* (London), 259 (1961); (d) see also E. A. Halevi, "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 109.

[9] Supplied by Merck Sharp and Dohme of Canada, Ltd.

[10] S. Seltzer, *J. Am. Chem. Soc.*, **87**, 1534 (1965); the ethanol-*d* was dried by azeotropic distillation from a benzene–alcohol–water mixture.