Mechanistic Studies in Organic Photochemistry. VI. Photodecarboxylation of Benzyl Esters

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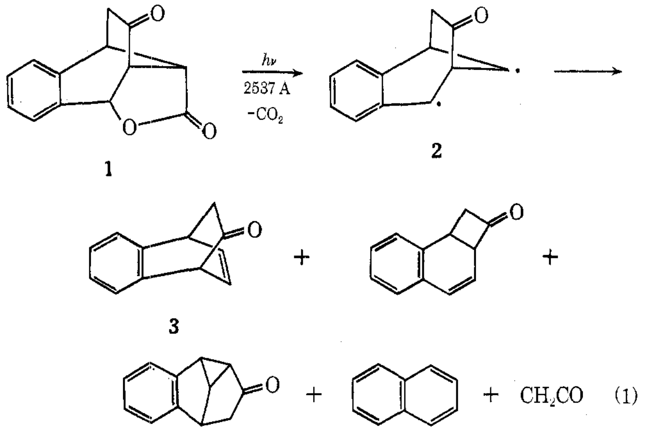
Irradiation of substituted γ-butyrolactones and substituted benzyl phenylacetates resulted in loss of CO_2 and formation of a carbon–carbon bond. Quantum yields for the reaction ranged from 0.03 to 0.25, depending on compound structure and the conditions of the reaction. The reaction could be sensitized with high-energy triplet sensitizers and quenched with cyclohexadiene, implicating the triplet excited state as the reactive state. Solvent effects, structural effects, effects of added nucleophiles, and the lack of stereospecificity for this reaction indicate radical intermediates prior to carbon–carbon bond formation. The similarity of solvent effects on the photostationary state of diphenylcyclopropanes (**13** and **14**) to those for the photodecarboxylation of diphenyllactones (**11** and **12**) implies a 1,3 diradical-like intermediate in the lactone reaction. Replacement of the benzyl moiety in benzyl phenylacetate with either an α-naphthyl or furfuryl moiety also resulted in photodecarboxylation. Allyl phenylacetate did not photodecarboxylate.

As part of our mechanistic study of the photorearrangements of benzobicyclo[2.2.2]octadienone (**3**), the lactone **1** was photolyzed in an effort to obtain the diradical **2**, a possible intermediate in triplet ketone rearrangement.[1a] We found that direct or sensitized irradiation of **1** resulted in a *quantitative* and efficient loss of carbon dioxide, leading to products arising from **2** (eq 1).[1] Decarboxylation is ordinarily a minor pathway in the solution photochemistry of lactones[2,3] and esters.[4-6]



1 **2** **3**

For simple esters, decarboxylation is one pathway available to the excited state; the relative importance of the process depends on the structure of the ester and the photolysis conditions.[4] Loss of carbon dioxide has been observed as the major photochemical pathway in the mercury-sensitized vapor-phase photolysis of simple lactones and butenolides,[5] the γ irradiation or photolysis of benzyl acetate in benzene solution,[6] photolysis of *p*-methoxybenzyl acetate,[7] and the photodecomposition of a dihydrosantonin.[8]

We wished to extend our study of the lactone **1** to simpler analogs to determine the importance of the strained bicyclic system and of the ketone function in the observed decarboxylation. Further, we hoped to develop synthetically useful applications of this process. To study the generality and utility of the reaction, a series of simple γ-phenyl-γ-butyrolactones and benzyl esters (the acyclic equivalent) was synthesized and their photochemistry studied.

Results and Discussion

Lactones. Preliminary Studies.—The simplest functional analog of lactone **1**, γ-phenyl-γ-butyrolactone[9] (**4**), upon direct irradiation (or acetone sensitization) led to loss of carbon dioxide and the formation of a single product in low yield. Continued irradiation led to product disappearance and polymer formation. The product was identified as phenylcyclopropane (**5**) by comparison of vpc, ir, and mass spectral data with those of an authentic sample.[10] To determine the influence of the phenyl substituent on the reaction pathway, the corresponding α-phenyl[11] (**6**) and β-phenyl[12] (**7**) derivatives were prepared and their photochemistry studied. Acetone-sensitized and direct irradiation of **6** and **7** gave no detectable carbon dioxide formation by the limewater test (a simultaneous photolysis of the γ isomer **4** showed considerable CO_2 evolution). These compounds were not investigated further.

In an effort to increase the yield of cyclopropane products and to evaluate the effect of other substituents on the lactone ring, α-cyano-γ-phenyl-γ-butyrolactone (**8**)[13] was prepared and photolyzed. Direct or sensitized irradiation of **8** also led to decarboxylation and the formation of two major products, *cis*- and *trans*-2-phenylcyclopropanecarbonitrile (**9** and **10**) by comparison with authentic samples. The yield of cyclopropane products was quite high; 44% of **9** and 48% of **10** were obtained from preparative photolysis in acetone at 2537 Å. The photochemistry of **4**, **6**, **7**, and **8** is presented in Chart I.

Since the lactone **8** could not be obtained in stereo-

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(1) (a) R. S. Givens and W. F. Oettle, *Chem. Commun.*, 1164 (1969); (b) R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, **93**, 3301 (1971).

(2) R. H. Linnell and W. A. Noyes, Jr., *ibid.*, **72**, 3963 (1950).

(3) (a) R. Simonaitis and J. N. Pitts, Jr., *ibid.*, **91**, 108 (1969); (b) *ibid.*, **90**, 1389 (1968); (c) J. N. Pitts, Jr., R. Simonaitis, and J. M. Vernon, *Tetrahedron Lett.*, 3209 (1965).

(4) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 434 ff.

(5) I. S. Krull and D. R. Arnold, *Tetrahedron Lett.*, 1247 (1969).

(6) W. Van Dusen, Jr., and W. H. Hamill, *J. Amer. Chem. Soc.*, **84**, 3648 (1962).

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(8) G. W. Perold and G. Ourisson, *Tetrahedron Lett.*, 3871 (1969).

(9) N. H. Cromwell, P. L. Creger, and K. E. Cook, *J. Amer. Chem. Soc.*, **78**, 4412 (1956).

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(11) (a) E. C. Knowles and J. B. Cloke, *J. Amer. Chem. Soc.*, **54**, 2028 (1932); (b) G. Pagliarini, G. Cignarella, and E. Testa, *Farmaco, Ed. Sci.*, **21**, 358 (1966).

(12) C. H. DePuy, F. W. Breitbeil, and K. L. Eilers, *J. Org. Chem.*, **29**, 2810 (1964).

(13) G. D. Zuidema, P. L. Cook, and G. Van Zyl, *J. Amer. Chem. Soc.*, **75**, 294 (1953).

CHART I

PHOTOCHEMISTRY OF α-, β-, AND γ-PHENYLBUTYROLACTONE (4, 6, 7) AND α-CYANO-γ-PHENYL-γ-BUTYROLACTONE (8)

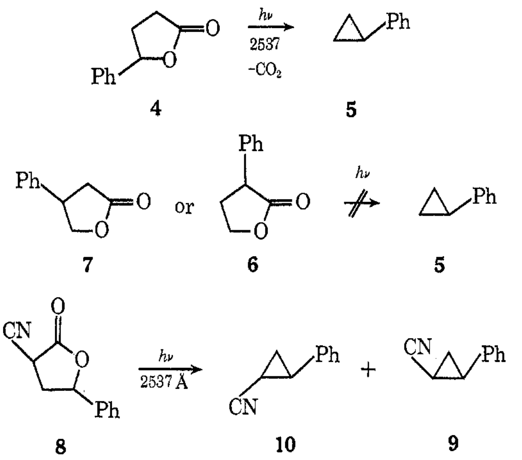
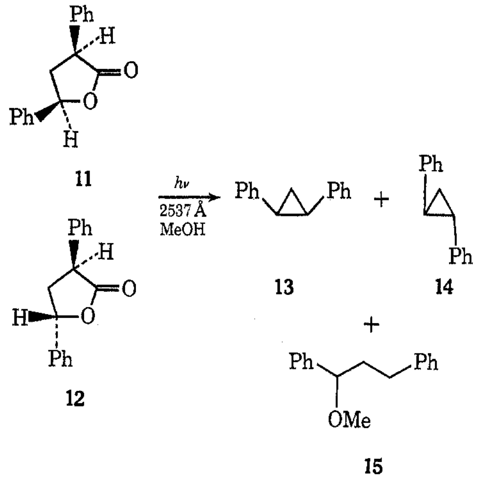


CHART II

PHOTOCHEMISTRY OF *cis*- AND *trans*-α,γ-DIPHENYL-γ-BUTYROLACTONE (11 and 12)



chemical purity, our study could not answer one question of paramount importance, *i.e.*, is the loss of CO_2 stereospecific? Stereospecificity might suggest a concerted process involving departure of CO_2 at the same time that the cyclopropane bond is formed,[14] while a lack of stereospecificity would require CO_2 loss followed by cyclopropane bond formation.

To resolve the concerted–nonconcerted question, the known[15] cis and trans isomers of α,γ-diphenyl-γ-butyrolactone (**11** and **12**) (Chart II) were prepared and studied. Photolysis of either **11** or **12** in methanol solution at 2537 Å led to the same mixture of three products (by vpc coinjection and by spectral analysis of the crude product mixtures). The products (in 50–60% yield) were isolated by column chromatography on silver nitrate–silica gel and characterized as *cis*-1,2-diphenylcyclopropane (**13**), the trans isomer **14**, and 1,3-diphenylpropyl methyl ether (**15**) by comparison with authentic samples.[16,17] The ether **15** was shown to be a product of secondary photolysis of **13** and **14**, since none of this compound could be detected by vpc at low conversion of **11**, while extended irradiation gave increased yields of **15** at the expense of **13** and **14**. Photolysis of lactones **11** and **12** in dioxane solvent gave only two major products, corresponding to the cyclopropanes. In all cases, however, minor amounts of secondary photoproducts of the cyclopropanes were observed; these have been described elsewhere.[18]

Observation of the isomeric cyclopropanes as primary photoproducts of both **11** and **12** at low conversion (Table I) suggests that CO_2 loss could not be a totally concerted process.

Lactones. Quantitative Results.—Quantitative studies of the photochemistry of the lactones were undertaken to obtain further information on the mechanism of the decarboxylation process. Quantum yields for disappearance, CO_2 evolution, and product appearance were determined (see Experimental Section for details) and are given in Table I.

TABLE I

QUANTUM YIELDS FOR DISAPPEARANCE, CO_2 EVOLUTION, AND PRODUCT APPEARANCE FOR γ-BUTYROLACTONES[a]

Lactone	dis[b,c]	CO_2[c,d]	Product[c]
γ-Phenyl (**4**)	0.026	0.020	0.0094 (**5**)
α-Cyano-γ-phenyl (**8**)	0.092	0.100	0.032 (cis, **9**) 0.045 (trans, **10**)
cis-Diphenyl (**11**)	0.045	0.026	0.010 (cis, **13**) 0.011 (trans, **14**)
trans-Diphenyl (**12**)	0.051 0.052 ± 0.005[e]	0.027	0.0064 (**13**) 0.0078 (**13**)[e] 0.0072 (**14**) 0.0075 (**14**)[e]

[a] Direct irradiation, dioxane solvent, 2537 Å. [b] Obtained by quantitative vpc. [c] Quantum yields at 20–30% conversion. The differences in quantum yields are due to the solvent addition products, which were not analyzed. [d] Trapped with tared Ascarite–Anhydrone scrubber. [e] Limiting values extrapolated to zero conversion.

The limiting value for the disappearance quantum yield of the *trans*-diphenyl lactone **12** indicates that secondary photolysis and internal quenching phenomena remain unimportant up to 30% conversion; the limiting values for the cyclopropanes **13** and **14** indicate that both are primary photoproducts.

In order to elucidate the effects of solvent on the mechanism, other solvents were utilized and these results are presented in Table II. In all cases, both lactones **11** and **12** gave both cyclopropanes **13** and **14** as primary photoproducts, although some solvents led to formation of several other products. Isomerization of the starting lactones was shown to be unimportant by vpc and by nmr analysis of recovered lactone from 20–30% conversion runs. These data clearly indicate that the reaction is primarily, if not completely, occurring *via* a nonconcerted pathway.

The results of the solvent study also indicate some effect of the solvent on the product ratio; there is, however, no clear pattern of retention *vs.* inversion or complete nonstereospecificity. In an effort to interpret the lactone solvent effects, the solvent effect on the photoequilibration of the cyclopropanes **13** and **14** was investigated.

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[14] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Aschaffenburg, Germany, 1970, p 65 ff.

[15] R. N. Johnson, J. B. Lowry, and N. V. Riggs, *Tetrahedron Lett.*, 5113 (1967). Communication of unpublished results on the synthesis and isolation of the α,γ-diphenyl lactone is gratefully acknowledged.

[16] S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

[17] C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, *J. Amer. Chem. Soc.*, **88**, 5675 (1966).

[18] G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965), and references cited therein.

TABLE II

SOLVENT EFFECTS ON DISAPPEARANCE QUANTUM YIELD[a] AND RATIO[a,b] OF *cis*- AND *trans*-CYCLOPROPANE FOR DIPHENYL LACTONES

Lactone	Solvent	ϕ_{dis}	% cis (13)
cis (11)	10% MeOH–ether	0.12	58
	CH_3CN	0.074	46
	i-PrOH	0.061	52
	Dioxane	0.045	48
	Acetone[c,d]	0.042	45
trans (12)	10% MeOH–ether	0.026	54
	CH_3CN	0.042	37
	i-PrOH	0.070	34
	Dioxane	0.051	47
	Acetone[c,d]	0.040	45
	Cyclohexane[c,f]	*e*	55
	Hexane[c,f]	*e*	50
	95% ethanol	*e*	41

[a] Determined by quantitative vpc; 5% conversion at 2537 Å. [b] Extrapolated to zero conversion. [c] Several other products formed; cyclopropanes *ca.* 60% of total. [d] Sensitizer. [e] Not determined. [f] Estimated from triangulated areas in vpc.

Several reports on the photoisomerization of *cis*- and *trans*-1,2-diphenylcyclopropane appear in the literature.[17–22] Hammond and coworkers showed that the isomerization could be sensitized,[19,20] but found that the sensitization process involved singlet energy transfer (for naphthalene derivatives) since the quantum yield for sensitization paralleled the quenching of the fluorescence from the sensitizer.[21] The cyclopropanes **13** and **14** also are found to undergo isomerization on direct irradiation.[17,18,22] Some results for direct irradiation in various solvents are shown in Table III.

TABLE III

SOLVENT EFFECTS ON THE PHOTOEQUILIBRATION OF 13 AND 14

Solvent	Photostationary state, % cis
10% MeOH–ether[a]	72
10% MeOH–ether[b]	72
CH_3CN[a]	59
i-PrOH[a]	70
Dioxane[a]	72
MeOH[a]	67
Benzene[c]	61
Cyclohexane[c]	61

[a] Excess **13**, 2537 Å. [b] Excess **14**, 2537 Å. [c] Reference 18.

Each solvent studied leads to a photostationary state favoring the cis cyclopropane **13** in accord with the literature reports.[17–22] Similarly, photolysis of synthetic samples of *cis*- and *trans*-2-phenylcyclopropanecarbonitrile (**9** and **10**) gave a photostationary state containing 53% cis and 47% trans (from pure **9** or pure **10**, direct irradiation at 2537 Å in ether).

Table III shows, however, that the relative composition of the photostationary state is influenced by the solvent, although the effect is small. Although this process is not a true photoequilibrium, since formation of other products becomes important at long conversion, depleting the system of cis and trans isomers at varying rates,[18,22] low-conversion studies should allow evaluation of the ratio of the rate constants for closure of the suggested diradical intermediate[18] to cis cyclopropane (k_c) to that for closure to trans cyclopropane (k_t). These values are obtained from the relation in eq 2, which relates the concentration of cis and trans isomers at the steady state to the ratio of extinction coefficients at the wavelength of photolysis and the k_c/k_t ratio.[23]

$$\frac{[\text{cis}]}{[\text{trans}]} = \frac{\epsilon_{\text{trans}}}{\epsilon_{\text{cis}}} \cdot \frac{k_c}{k_t} \tag{2}$$

Assuming that other photochemical processes are unimportant at short times and that thermal isomerization[24] is prevented by solvent deactivation, the solvent effect on the photostationary state should arise from effects on the k_c/k_t ratio or on the extinction coefficient ratio. Determination of the ratios of ϵ's gives the k_c/k_t ratio as a function of solvent (Table IV).

TABLE IV

COMPARISON OF $k_{\text{cis}}/k_{\text{trans}}$ FOR PHENYL LACTONE PHOTOLYSES AND k_c/k_t FOR DIPHENYLCYCLOPROPANE PHOTOEQUILIBRIUM

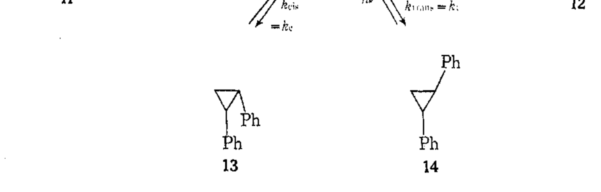
Solvent	$k_{\text{cis}}/k_{\text{trans}}$	k_c/k_t
	cis-Diphenyl (11)	
10% MeOH–ether	1.38	0.63
CH_3CN	0.85	0.38
i-PrOH	1.08	0.54
Dioxane	0.92	0.52
	trans-Diphenyl (12)	
10% MeOH–ether	1.17	0.63
CH_3CN	0.59	0.38
i-PrOH	0.52	0.54
Dioxane	0.89	0.52
Cyclohexane	1.22	0.35 (1.00)[a]
	Cyanophenyl (8)	
Ether	0.67	0.71

[a] Reference 22, assuming that both diphenylcyclopropanes give the same intermediate.

The per cent composition of cyclopropane products from the lactones (at zero conversion) gives the $k_{\text{cis}}/k_{\text{trans}}$ ratio directly (Chart III). If product formation in the lactones results from the same intermediate involved in the isomerization, the $k_{\text{cis}}/k_{\text{trans}}$ ratio should equal the k_c/k_t ratio for the cyclopropanes. This

CHART III

PROCESSES INVOLVED IN PHOTOLYSIS OF DIPHENYL LACTONES AND DIPHENYL CYCLOPROPANES



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(19) G. S. Hammond, P. Wyatt, C. D. De Boer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964).

(20) G. S. Hammond and R. S. Cole, *ibid.*, **87**, 3256 (1965).

(21) S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968).

(22) E. W. Valyocsik and P. Sigal, *J. Org. Chem.* **36**, 66 (1971).

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

(24) L. B. Rodewald and C. H. DePuy, *Tetrahedron Lett.*, 2951 (1964), and references cited therein.

equality holds if the singlet diradical and triplet diradical either are in equilibrium before closure to the cyclopropanes (a reasonable assumption in light of the reported[25] energy difference of ≤ 1 kcal for 1,3-diradicals) or have identical rate ratios for closure to the cis and trans cyclopropanes. The values for k_c/k_t and k_{cis}/k_{trans} are listed in Table IV.

In fact, as shown in Table IV, k_{cis}/k_{trans} varies from one to three times the k_c/k_t ratio. It is apparent, however, that the solvent effects show a qualitative parallel between the lactone photolyses and the diphenylcyclopropane photostationary state. Further, the similarity of the rate ratios for the lactones in all solvents studied suggests that the intermediate involved is neutral, rather than highly polar; it seems unlikely that a polar species would give the same relative yields of diphenyl cyclopropanes over a wide solvent polarity range.

The solvent effects listed in Table II for the ratio of diphenylcyclopropanes from the diphenyl lactones would appear, consequently, to originate in solvent effects on closure of the intermediate, rather than a change in mechanism with solvents. The origin of the solvent effect on the quantum yields of disappearance cannot be determined without further study, but presumably results from changes in rates of deactivation or intersystem crossing.

The discrepancy in the k_{cis}/k_{trans} and k_c/k_t ratios is not clearly understood. There are, however, three possible origins: (1) photoisomerization of the diphenylcyclopropanes and photodecarboxylation of the diphenyl lactones do not involve the same intermediate; (2) the cis and trans lactones lead to different intermediates (as has been proposed for the diphenylcyclopropane isomerization[22]); or (3) the photostationary state method does not lead to correct values for the k_c/k_t ratios. Further study will be necessary to determine the exact origin of the discrepancy in rate ratios, but the third possibility (above) seems most likely. The photochemistry of the diphenylcyclopropanes is complicated by several competing processes, and the absolute rates of formation of *cis*-1,2-diphenylcyclopropane from *trans*- and of *trans*- from *cis*- have not been determined (although Valyocsik and Sigal[22] report that the quantum yields for these processes are the same). It is possible that the photostationary state concentrations of cis and trans isomers do not accurately reflect the ratio of k_c and k_t.

The results obtained from photolysis of the various lactones (*vide supra*) permit several mechanistic conclusions: (1) efficient decarboxylation requires that the excited aromatic chromophore be adjacent to the γ_{CO} bond (since the α- and β-phenyl isomers **6** and **7** show no tendency to decarboxylate); (2) either cleavage of the γ_{CO} bond is irreversible or recombination is faster than bond rotation, since recovered diphenyl lactones show no stereoisomerization; and (3) CO_2 loss leads to a 1,3 diradical which can close to give both isomeric cyclopropane products (in the α,γ-disubstituted lactones.)

Esters. Preliminary Results.—Our studies on lactone photochemistry (*vide supra*) showed that photodecarboxylation is a general phenomenon for γ-phenyl γ-lactones. Since the diphenyl lactones **11** and **12** were found to decarboxylate with good efficiency, the acyclic isomers, benzyl phenylacetates, might also be expected to undergo photodecarboxylation.

The parent compound, benzyl phenylacetate (**16**), was readily obtained by the esterification of phenylacetic acid with benzyl alcohol and purified by distillation. Photolysis (Hanovia 450-W mercury arc, ≥ 2400 Å) in dioxane led to CO_2 expulsion and one major product in good yield by vpc analysis. Column chromatography gave 32% yield of dibenzyl (**17**) (57% based on recovered ester), a 44% yield of recovered **16**, and a mixture of high-polarity products. The dibenzyl was identified by spectral comparison, melting point, and mixture melting point with an authentic sample.[26] Similarly, the *p,p'*-dimethyl (**18**) and *p,p'*-dimethoxy (**19**) isomers were prepared and photolyzed; these also expelled CO_2 to give the corresponding dibenzyls, **20** and **21**, as products.

To test our earlier conclusion that a free diradical intermediate was involved in the photodecarboxylation process, the unsymmetrical ester, *p*-methylbenzyl *p*-methoxyphenylacetate (**22**), was synthesized and photolyzed. Again, CO_2 loss was observed, but vpc analysis indicated three products. These were isolated by column chromatography and preparative vpc and identified as **20**, *p*-methoxy-*p'*-methyldibenzyl (**23**), and **21** in a ratio of 1:2.5:1, respectively. The overall yield at 63% conversion was 99% based on recovered starting ester. These results are again in agreement with a radical process involving free intermediates, since a concerted process should lead to a greater yield of unsymmetrical product. These results are summarized in Chart IV.

As a further test of the generality and mechanistic course of the decarboxylation, meta-substituted derivatives were examined to determine if Zimmerman's[7] observation of a change in mechanism for benzyl acetates, from free radical to ionic processes,[7] would be duplicated in the benzyl phenylacetates.

The unsymmetrical di-meta-substituted derivatives **24** and **25** (Chart IV) were photolyzed in 20% aqueous dioxane at 2537 Å. Neither isomer showed any change in mechanism; both gave a mixture of the three possible dibenzyls (**26**, **27**, and **28**). No alcohol products, expected from trapping of an ionic intermediate by the water, could be observed by vpc or isolation of the photoproducts. These results again support a free-radical mechanism for decarboxylation. The dibenzyls, after isolation, were obtained in 60% yield (from **24**) and 74% yield (from **25**) based on recovered starting ester.

Esters **24** and **25** also were photolyzed in methanol saturated with sodium acetate ($\sim 1.4\ M$) in an effort to detect photosolvolysis products. Ester **24** showed no change in photochemical behavior as compared to a sample photolyzed in dry dioxane; the three dibenzyls **26**, **27**, and **28** comprised >95% of the volatile products. Ester **25**, however, showed five new products after irradiation (two major and three minor) in a combined yield of 20% of the volatile products, while the dibenzyls were formed in 80% yield; the ester was completely converted to products after 500 min. An

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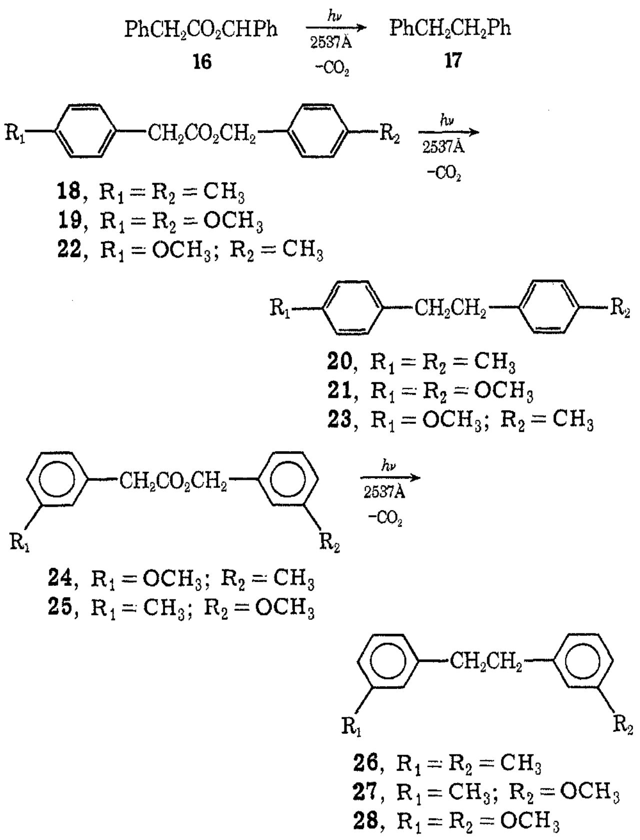
[25] (a) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 7227 (1970); (b) G. L. Closs, *ibid.*, **91**, 4552 (1969), and references cited therein.

[26] Authentic samples provided by Professor J. A. Landgrebe are gratefully acknowledged.

Chart IV

Photochemistry of Benzyl Phenylacetate (16) and Substituted Derivatives



identical dark reaction of **25** resulted in 80% conversion of the ester in 420 min, with formation of two major products. These had the same retention times as the major new products in the photolysis sample (by vpc coinjection), suggesting that the additional products resulted from ground-state solvolysis, rather than a change in mechanism in the photolysis. This result supports the conclusion that radical formation and recombination, rather than a polar mechanism, is favored for the benzyl phenylacetates.

Since decarboxylation was found to be a general phenomenon for various benzyl phenylacetates, it was of interest to study esters of other aromatic or radical-stabilizing alcohols such as the allyl (**29**), furfuryl (**30**), and α-naphthylmethyl (**31**) esters of phenylacetic acid.

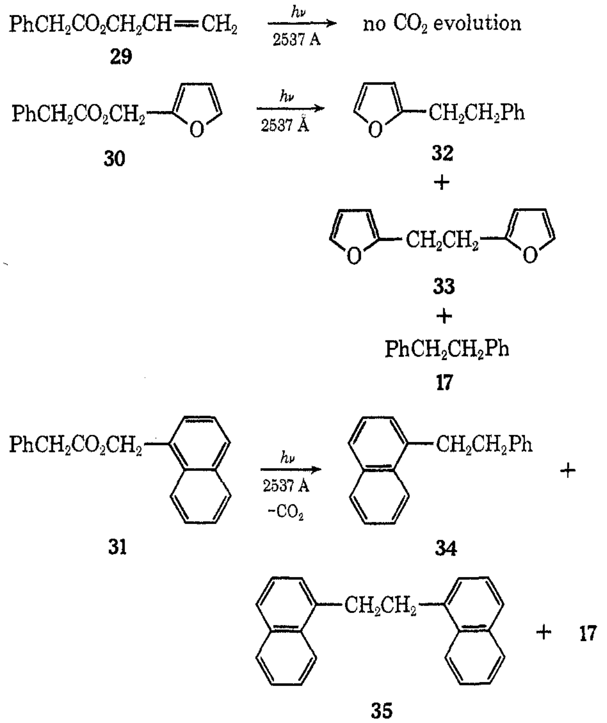
Photolysis of **29** under the usual conditions (dioxane solvent, 2537 Å) gave no detectable CO_2 evolution (limewater test), while vpc analysis indicated the formation of at least nine products, which were not investigated further.

The furfuryl ester **30**, however, did undergo decarboxylation upon direct irradiation (2537 Å) to give the three possible radical coupling products **17**, **32**, and **33** (Chart V).

The α-naphthylmethyl ester **31** was studied at both 2537 and 3000 Å, since the naphthalene chromophore will absorb at longer wavelengths than the chromophores previously employed. Irradiation at 2537 Å gave three products by vpc analysis, in a 1:10:1 ratio. These were isolated and characterized as 1-(α-naphthyl)-2-phenylethane (**34**), 1,2-di-α-naphthylethane (**35**), and dibenzyl (**17**), respectively. At 3000 Å, however, the product ratio had changed to 1:13:1.

Chart V

Irradiation of Phenylacetates



The results for these three systems (Chart V) show that photodecarboxylation is a general process for esters of alcohols which are conjugated with aromatic or heteroaromatic systems.

Esters. Quantitative Studies.—Further mechanistic information was obtained by determination of the quantum yields for various benzyl phenylacetates. These values are presented in Table V.

Table V

Quantum Yields[a] for Photolysis of Substituted Benzyl Phenylacetates

Ester	ϕ_{CO_2}[b,c]	ϕ_{dis}[d]	$\phi_{product}$[d]
16	0.031	0.033	0.023 (17)
18	e	0.25	0.22 (20)
19	0.19	0.25	0.21 (21)
24	e	0.075	0.012 (26)
			0.044 (27)
			0.012 (28)
25	e	0.23	0.028 (26)
			0.19 (27)
			0.032 (28)

[a] Direct irradiation, 2537 Å. [b] Trapped with tared Ascarite-Anhydrone scrubber. [c] Quantum yields at 20–30% conversion. [d] Obtained by quantitative vpc. [e] Not determined.

In all cases, the efficiency of decarboxylation is at least as high as that of the lactones. Both methyl and methoxy substituents lead to higher quantum yields as compared to the unsubstituted compounds. The efficiency of these reactions is within the range of synthetically useful processes.

Although the efficiency of the reaction is good, the formation of cross-coupling products reduces the synthetic potential. In an effort to overcome this problem, the effect of various solvents was studied, in an effort to take advantage of the "cage effect," which has been extensively studied in free-radical systems.[27] The results for photolysis of *p*-methylbenzyl *p*-methoxyphenylacetate (**22**) are shown in Table VI.

TABLE VI

SOLVENT EFFECTS ON PRODUCT COMPOSITION FROM DIRECT IRRADIATION[a] OF **22**[b]

Solvent	Di-*p*-CH_3 (**20**), %	*p*-OCH_3-*p*'-CH_3 (**23**), %	Di-*p*-OCH_3 (**21**), %
t-BuOH	15	68	17
95% EtOH	22	62	16
i-PrOH	14	71	15
Isooctane	20	61	19
Methylcyclohexane	22	61	17

[a] RPR-2537 Å lamps. [b] Determined by triangulation from vpc trace.

Table VI indicates that the yield of unsymmetrical product is highest in the alcohol solvents, while the hydrocarbon solvents lead to higher yields of cross-coupling products. In addition, it was observed that the efficiency of the process is highest for *tert*-butyl alcohol, followed by 95% ethanol and isopropyl alcohol. As has been noted in the lactone photolyses (*vide supra*), decarboxylation was much less efficient in hydrocarbon solvents and additional products were observed in the vpc trace.

To confirm the vpc results, a preparative photolysis of **22** was performed in isopropyl alcohol. Column chromatography and nmr analysis of the mixture indicated a 17:66:17 weight per cent ratio of products **20**, **23**, and **21**, respectively (60% yield based on recovered ester).

Results for lactone **1**[1] indicate that the decarboxylation process occurs *via* the triplet state, since the reaction can be sensitized with acetone, acetophenone, and benzophenone, and can be quenched with 1,3-cyclohexadiene. As shown above, the simpler lactones undergo decarboxylation upon sensitization with acetone, but at reduced efficiency. To determine the multiplicity involved in these simpler systems, the α-naphthyl ester **31** was investigated further.

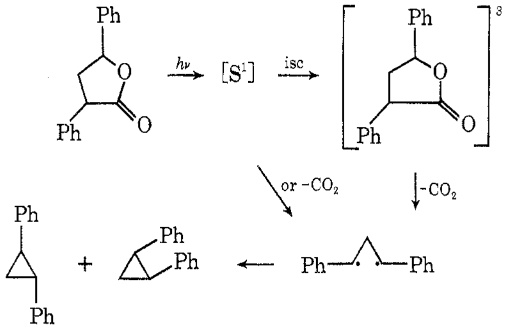
The decarboxylation of ester **31** was quenched by 1,3-cyclohexadiene upon irradiation at 3130 Å. Formation of new products and low conversion precluded complete analysis of the quenching, but a Stern–Volmer plot for 1-(α-naphthyl)-2-phenylethane gave a slope of 43.6 l./mol, leading to a value of τ of 8.5×10^{-9} sec. Uv analysis indicated that the ester absorbed >99% of the light. These results suggest the involvement of the triplet state of **31**, although the observed lifetime of the excited state is shorter than typical triplet lifetimes.

From our study of the photodecarboxylation of benzyl esters and γ-lactones, we conclude that this process is general for esters (and lactones) in which an aromatic (or heteroaromatic) chromophore is conjugated with the ethereal C–O bond of the ester or lactone. Electron-donating substituents on the aromatic ring increase the efficiency of decarboxylation relative to benzyl phenylacetate. The quantum yields for the esters are within the range of synthetically useful processes.

The mechanistic studies above and previous results[28] lead us to conclude that the photodecarboxylation process observed occurs *via* discrete radical (diradical) intermediates which are formed by stepwise loss of CO_2, possibly from the triplet state of the ester or lactone, followed by recombination of the radicals (diradical) to give the observed products. Meiggs and Miller[28] have detected benzyl radicals in their study of the photolysis of methyl phenylacetate in agreement with our findings. The detailed mechanistic pathway is exemplified in Chart VI.

CHART VI

MECHANISM OF PHOTODECARBOXYLATION FOR LACTONES AND ESTERS



Experimental Section[29]

A. **Synthesis.** **γ-Phenyl-γ-butyrolactone (4).**—This was prepared by the method of Cromwell, *et al.*[9]

Phenylcyclopropane (5).—This was prepared by the method of Peterson and Skell.[10]

α-Phenyl-γ-butyrolactone (6).—This was prepared by the method of Pagliarini, *et al.*[11b]

β-Phenyl-γ-butyrolactone (7).—This compound was obtained by hydrolysis and decarboxylation[12] of a mixture of α-cyano-β-phenyl and α-cyano-γ-phenyl lactones prepared by reaction of styrene oxide with ethyl cyanoacetate.[13]

α-Cyano-γ-phenyl-γ-butyrolactone (8).[13]—Sodium metal (5.75 g, 0.25 g-atom) was dissolved in absolute ethanol (100 ml) under nitrogen in a flask fitted with mechanical stirring, dropping funnel, and reflux condenser with drying tube. The solution was cooled in ice, and ethyl cyanoacetate (28.3 g, 0.25 mol) was added during 10 min. Styrene oxide (30.0 g, 0.25 mol) was then added dropwise during 30 min. The solution was allowed to come to room temperature and stirred overnight, then heated to 60° for 8 hr. The excess ethanol was removed *in vacuo* and 100 ml of benzene was added to the residue, followed by 50 g of ice and 25 ml of concentrated HCl. The aqueous layer was washed with 4 × 100 ml of benzene, and the benzene solution was dried over magnesium sulfate and evaporated to afford 26.7 g (57%) of a mixture of the β-phenyl and γ-phenyl isomers[12] as a white crystalline solid, mp 73–82°. This was recrystallized repeatedly from 95% ethanol to give 1.5 g of white solid, mp 131–132°, assigned the structure α-cyano-γ-phenyl-γ-butyrolactone (**8**) from spectral evidence: nmr (acetone-d_6, TMS) δ 7.20 (m, 5 H), 5.48 (m, 1 H), 4.20 (m, 1 H), 2.64 (m, 2 H); ir (KBr) 4.40 (m), 5.62, 7.41, 8.48, 10.00, 10.72, 13.10, 14.25 μ (s); mass spectrum *m/e* (rel intensity) 187 (93), 143 (49), 116 (39), 115 (39), 107 (60), 105 (100), 79 (25), 78 (87), 77 (80), 52 (27), 51 (53), 50 (21), 39 (25); uv (95% ethanol) λ_{max} 2680 Å (ϵ 120), 2640 (210), 2580 (230), 2520 (180), 2480 sh (120), 2420 sh (90).

***cis*- and *trans*-2-Phenylcyclopropanecarbonitrile (9 and 10).**[30]—

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[27] S. F. Nelson and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 143 (1966).

[28] T. O. Meiggs and S. I. Miller, *ibid.*, **94**, 1989 (1972).

[29] Melting points were obtained on a hot-stage apparatus calibrated with known samples, unless otherwise noted. Boiling points are uncorrected. The following spectrometers were used: nmr, Varian A-60; ir, Beckman IR-8; uv, Cary 14; mass, Varian MAT CH-2.

[30] M. Horak, J. Smejkal, and J. Farkas, *Collect. Czech. Chem. Commun.*, **28**, 228 (1963).

cis-2-Phenylcyclopropanecarboxylic acid[26] (516 mg, 3.18 mmol) was dissolved in 5 ml of 1 *N* sodium hydroxide and the water was removed under vacuum. Reagent, dry benzene (40 ml) was added, followed by 411 mg (3.23 mmol) of oxalyl chloride and two drops of pyridine. After the solution was stirred for 2 hr, 100 ml of cold concentrated ammonia was added, with stirring and ice cooling. The product mixture was extracted with 5 × 100 ml of ether and the ether extracts were dried and evaporated to give 383 mg (75%) of crude amide, nmr (CDCl$_3$, TMS) δ 7.3 (s), 2.0–0.8 (m), 0.7–0.4 (m). The crude amide was dissolved in 25 ml of dry reagent benzene, 5 ml of thionyl chloride was added, and the resulting solution was stirred at reflux for 5 hr and then poured into 50 ml of ice-cold concentrated ammonia. Extraction with 5 × 50 ml of ether gave 170 mg (50%) of crude *cis*-2-phenylcyclopropanecarbonitrile, which was chromatographed on a 1.9 × 30 cm column of Florisil to give 83 mg of pale yellow oil (fractions 13–30, 2% ether–hexane eluent). Preparative tlc (Merck silica gel F$_{254}$, 10% ethyl acetate–benzene, and micro distillation (90°, 40 mm) give the nitrile **9** as a water-white liquid: nmr (CCl$_4$, TMS) δ 7.28 (s, 5 H), 2.39 (d of d, 1 H), 1.50 (m, 3 H), ir (CCl$_4$) 3.21 (sh), 3.23 (sh), 3.26 (m); 4.43 (s); 6.25, 6.64, 6.85 (m); 7.24, 7.47, 8.59, 8.93, 9.22, 9.48 (w), 9.66, 10.42 (m), 11.00, 12.05, 13.88 (sh w), 14.40 (s); 14.70 (sh w), 15.80 μ (w).

Similarly the trans isomer **10** was prepared from 502 mg (3.1 mmol) of the corresponding acid.[26,30] The crude amide (411 mg, 70%) had nmr (CDCl$_3$, TMS) δ 7.25 (m), 1.80–1.10 (m), 0.55 (m); ir (KBr) 2.97, 3.12, 6.13 (s), 6.92, 7.00, 13.38, 14.45 μ (m). Dehydration as above gave 295 mg (95%) of crude **10** purified by preparative tlc as above and sublimation (90°, 30 mm): mp 51–52° (capillary) (lit.[30] mp 49.5°); nmr (CCl$_4$, TMS) δ 7.18 (m, 5 H), 2.56 (m, 1 H), 1.48 (m, 3 H); ir (CCl$_4$) 3.21 (sh); 3.32, 3.27 (m); 4.44 (s); 6.21, 6.67, 6.85, 6.90 (sh, m); 7.19, 8.20, 8.51, 8.89 (w); 9.26, 9.48, 9.71, 10.64 (m); 10.81, 11.11, 13.89 (sh w); 14.39 μ (s).

***cis*- and *trans*-α,γ-Diphenyl-γ-butyrolactone (11 and 12).**—These were prepared by the method of Johnson and Riggs[15] as follows.

4-Oxo-2,4-diphenylbutyronitrile.[31]—This was prepared by the method of Davey and Tivey.[32]

4-Oxo-2,4-diphenylbutyric Acid.—The nitrile from above (90.0 g, 0.38 mol) was heated under reflux with a mixture of 300 ml of concentrated sulfuric acid, 400 ml of glacial acetic acid, and 120 ml of water. The mixture was cooled and poured onto crushed ice; the precipitate was filtered off and dissolved in ether. Extraction with bicarbonate solution followed by acidification of the extract with concentrated HCl gave 77.3 g (85%) of the acid, mp 152–155° after recrystallization from THF–hexane (lit.[15] mp 151.5–152.5°).

***cis*- and *trans*-α,γ-Diphenyl-γ-butyrolactone (11 and 12).**—To a solution of 31.5 g (0.13 mol) of the butyric acid in 500 ml of dry THF was added 15.6 g (0.69 mol) of lithium borohydride in 500 ml of THF; the solution was stirred overnight under nitrogen. Water (600 ml) was added carefully, followed by 300 ml of 10% sulfuric acid. The THF was removed *in vacuo* and the residual solution was extracted with ether to give 26.0 g (84%) of crude product, which was chromatographed on a 4.5 × 110 cm column of Davison Grade 950 silica gel, slurry packed with hexane, to afford (1-l. fractions): fractions 1 and 2, hexane eluent, nil; 3 and 4, 2% ether–hexane, nil; 5 and 6, 5% ether–hexane, nil; 7–19, 10% ether–hexane, 360 mg of residue; 20–28, 15% ether–hexane, 9.615 g of **12**; 29 and 30, 15% ether–hexane, 38 mg of a mixture of **11** and **12**; 31–46, 15% ether–hexane, 7.718 g of **11**.

The *cis*-α,γ-diphenyl-γ-butyrolactone (**11**) was crystallized from acetone–hexane, mp 106–107° (lit.[15] mp 107–107.5°). The trans isomer **12** was recrystallized from ether–hexane, mp 68–69° (lit.[15] mp 74°).

***cis*- and *trans*-1,2-Diphenylcyclopropane (13 and 14).**—These were prepared by the method of Beech, Turnbull, and Wilson.[16]

1,3-Diphenylpropyl Methyl Ether (15).—This was prepared according to the procedure of Irving, *et al.*[17]

Benzyl Phenylacetate (16).—This was prepared by the method of Wiessberger and Kibler.[33]

***p*-Methoxybenzyl *p*-Methoxyphenylacetate (19).**—This was prepared as above from 5.002 g (0.036 mol) of anisyl alcohol, 6.609 g (0.040 mol) of *p*-methoxyphenylacetic acid, and 106 mg of *p*-toluenesulfonic acid in 50 ml of benzene. After 3 hr, removal of the solvent gave 7.344 g (76%) of crude **18** as an off-white solid, mp 54–64°. The ester was recrystallized twice from acetone at Dry Ice temperatures to give 2.159 g of white needles, mp 66.5–67.5°. The recovered crude ester was recrystallized twice from 95% ethanol to give 2.449 g of lustrous plates: mp 68.5–69.0°; nmr (CDCl$_3$, TMS) δ 7.08 (m, 8 H), 5.08 (s, 2 H), 3.78 (s, 6 H), and 3.58 (s, 2 H); ir (CHCl$_3$) 3.27, 3.32 (sh); 3.36, 3.38 (m); 3.42 (s); 3.50 (m); 5.82, 6.21 (s); 6.31 (m); 6.65, 6.88, 6.95 (s); 7.05 (s); 7.30 (m); 7.70 (s); 8.20 (broad, s); 8.52 (sh); 8.80(s); 9.00 (sh); 9.72 (s); 10.80 μ (m); uv (dioxane) λ_{max} 2810 Å sh (ε 2640), 2750 (3120); mass spectrum (70 eV) *m/e* (rel intensity) 286 (10), 122 (24), 121 (100).

Anal. Calcd for C$_{17}$H$_{18}$O$_4$: C, 71.31; H, 6.34. Found: C, 71.48; H, 6.35.

***p*-Methylbenzyl *p*-Methylphenylacetate (18).**—The ester was prepared as above by acid-catalyzed dehydration of 3.000 g (0.020 mol) of *p*-methylphenylacetic acid, 2.440 g (0.020 mol) of *p*-methylbenzyl alcohol, and 208 mg of *p*-toluenesulfonic acid in 70 ml of benzene. Work-up as before and distillation gave 4.655 g (92%) of **19** as a water-white liquid, bp 137–141° (0.2 mm), which solidified in the receiver. The ester was recrystallized from 95% ethanol to constant melting point, 39.5–40°: nmr (CCl$_4$, TMS) δ 7.06 (s), 7.03 (s, 8 H), 4.98 (s, 2 H), 3.48 (s, 2 H), 2.30 (s, 6 H); ir (CCl$_4$) 3.20 (sh w); 3.25 (sh), 3.29, 3.36, 3.39, 3.45 (sh m); 5.30, 5.75 (sh), 6.20 (w); 6.61, 6.82 (sh), 6.90, 7.02 (sh), 7.25, 7.50, 7.70 (m); 8.00, 8.25 (s); 8.45 (m), 8.75 (broad, s), 9.75 (sh), 9.90 (sh), 10.18 (m); 10.62 μ (w); uv (dioxane) λ_{max} 2730 Å (ε 490), 2680 sh (480), 2640 (560), 2590 sh (420); mass spectrum (70 eV) *m/e* (rel intensity) 254 (10), 106 (29), 105 (100), 79 (23), 77 (31).

Anal. Calcd for C$_{17}$H$_{18}$O$_2$: C, 80.28; H, 7.13. Found: C, 80.48; H, 7.11.

***p*-Methylbenzyl *p*-Methoxyphenylacetate (22).**—Dehydration of a mixture of 5.003 g (0.041 mol) of *p*-methylbenzyl alcohol and 6.807 g (0.041 mol) of *p*-methoxyphenylacetic acid with 138 mg of *p*-toluenesulfonic acid catalyst in 35 ml of benzene gave 10.059 g (91%) of crude **22** which was distilled (177–183°, 1.0 mm), then recrystallized from ether at Dry Ice temperatures to give 5.379 g of **22** as white needles: mp 32–32.5°; nmr (CCl$_4$, TMS) δ 7.08 (s), superimposed on 6.92 (m, 8 H), 5.00 (s, 2 H), 3.71 (s, 3 H), 3.48 (s, 2 H), 2.32 (s, 3 H); ir (CCl$_4$) 3.31 (sh, m); 3.39 (s); 3.50 (m); 5.80, 6.20 (s); 6.30 (m); 6.63, 6.90, 7.30 (s); 7.60 (sh, m); 7.75, 8.15, 8.50, 8.85, 9.65, 10.25 (s); uv (95% ethanol) λ_{max} 2820 Å (ε 1310), 2750 (1540); mass spectrum (70 eV) *m/e* (rel intensity) 270 (17), 121 (100), 105 (67), 91 (54).

Anal. Calcd for C$_{17}$H$_{18}$O$_3$: C, 75.53; H, 6.72. Found: C, 75.76; H, 6.88.

***m*-Methylbenzyl *m*-Methoxyphenylacetate (24).**—As before, the ester was prepared by dehydration of 6.651 g (0.040 mol) of *m*-methoxyphenylacetic acid and 4.888 g (0.040 mol) of *m*-methylbenzyl alcohol with 188 mg of *p*-toluenesulfonic acid catalyst in 50 ml of benzene. Work-up and vacuum distillation gave 7.816 g (72%) of **24** as a water-white liquid: bp 158–160° (0.1 mm); nmr (CCl$_4$, TMS) δ 7.12 (m), 6.72 (m, 8 H), 4.98 (s, 2 H), 3.62 (s, 3 H), 3.49 (s, 2 H), 2.26 (s, 3 H); ir (CCl$_4$) 3.28, 3.31, 3.37, 3.51 (m); 5.77, 6.28, 6.31, 6.72, 6.85, 6.89, 6.99 (s); 7.30 (m); 8.00, 8.78 (s); 9.18, 9.25 (w); 9.50, 9.58 (s); 10.18, 11.43 (m); 14.52 μ (s); uv (dioxane) λ_{max} 2810 Å sh (ε 1900), 2730 (2270); mass spectrum (70 eV) *m/e* (rel intensity) 270 (21), 122 (73), 121 (47), 107 (32), 105 (100), 93 (22), 79 (36), 78 (21), 77 (46), 65 (24).

Anal. Calcd for C$_{17}$H$_{18}$O$_3$: C, 75.52; H, 6.72. Found: C, 75.53; H, 6.44.

***m*-Methoxybenzyl *m*-Methylphenylacetate (25).**—Using the general procedure above, 5.529 g (0.040 mol) of *m*-methoxybenzyl alcohol, 6.001 g (0.040 mol) of *m*-methylphenylacetic acid, and 273 mg of *p*-toluenesulfonic acid in 50 ml of benzene gave (after work-up and distillation) 6.968 g (65%) of **25**: bp 163–166° (0.1 mm); nmr (CCl$_4$, TMS) δ 7.00 (m), 6.75 (m, 8 H), 4.98 (s, 2 H), 3.61 (s, 3 H), 3.48 (s, 2 H), 2.25 (s, 3 H),; ir (CCl$_4$) 3.28, 3.31, 3.37, 3.51 (m); 5.77, 6.28, 6.31, 6.72, 6.85, 6.89, 6.99 (s); 7.30 (m); 8.00, 8.78 (s); 9.18 (w); 9.50, 9.58 (s); 10.18, 11.43 (m); 14.52 μ (s); uv (dioxane) λ_{max} 2810 Å sh (ε 1920), 2730 (2280); mass spectrum (70 eV) *m/e* (rel intensity) 270 (24), 138 (70), 122 (21), 121 (100), 105 (85), 91 (30), 77 (24).

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(31) E. P. Kohler and H. M. Chadwell, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 78.

(32) W. Davey and D. J. Tivey, *J. Chem. Soc.*, 1230 (1958).

(33) A. Weissberger and C. J. Kibler, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1943, p 610.

Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.52; H, 6.72. Found: C, 75.26; H, 6.63.

Allyl Phenylacetate (29).[34]—Phenylacetic acid (20.0 g, 0.15 mol) was dissolved in 150 ml of 1 *N* sodium hydroxide and the water was removed under vacuum. Benzene (300 ml) was added and the flask was fitted with a reflux condenser, addition funnel, and nitrogen inlet; then 19.872 g (0.16 mol) of oxalyl chloride was added dropwise. The solution was stirred for 3 hr (until gas evolution ceased), then divided into three equal parts. One portion of the solution was added slowly to a solution of 2.865 g (0.049 mol) of freshly distilled allyl alcohol in 50 ml of pyridine (distilled from barium oxide) in an ice bath. After stirring for 3 hr, the solution was poured into 200 ml of ice water and the aqueous layer was discarded. The benzene solution was washed with 200 ml of 10% sulfuric acid, 2 × 200 ml of 10% sodium bicarbonate, 200 ml of water, and 200 ml of brine, dried, and evaporated to give 4.871 g of crude ester which was distilled to give 3.223 g (37%) of **29**, bp 115–117° (10 mm) [lit.[34] bp 123° (15 mm)].

Furfuryl Phenylacetate (30).—A second portion of the phenylacetyl chloride solution (above) was added slowly to a pyridine solution of 4.812 g (0.049 mol) of freshly distilled furfuryl alcohol. The reaction mixture was worked up as above to give 8.839 g of material which, after distillation, afforded 4.857 g (46%) of **30**, bp 125–129° (0.6 mm), as a pale yellow oil. Treatment with decolorizing carbon gave the ester as a water-white liquid which yellowed rapidly: nmr (CCl_4, TMS) δ 7.22 (m, 1 H), 7.12 (s, 5 H), 6.20 (m, 2 H), 4.93 (s, 2 H), 3.44 (s, 2 H); ir (CCl_4) 3.20 (sh); 3.24 (sh); 3.28, 3.37 (sh w); 5.75 (s); 6.23 (w); 6.68 (m); 6.90, 6.98, 7.08 (sh, w); 7.32, 7.55 (sh); 7.32 (sh, m); 8.10, 8.70 (sh), 8.83 (s); 9.30 (w); 9.85 (sh), 10.25, 10.90 (m); 11.30 (w); 14.10 (sh), 14.42 μ (m); uv (95% ethanol) λ_{max} 2680 Å (ϵ 80), 2640 (160), 2470 (210), 2520 (170), 2470 (150); mass spectrum (70 eV) *m/e* (rel intensity) 216 (6), 91 (25), 81 (69), 31 (100), 29 (76).

Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 71.94; H, 5.36.

α-Naphthylmethyl Phenylacetate (31).—α-Naphthylmethanol was synthesized by reduction of 20.014 g (0.128 mol) of 1-naphthaldehyde with 2.476 g (0.065 mol) of $LiAlH_4$ in 400 ml of ether. After stirring for 30 min, the reaction was worked up to give 20.520 g of alcohol as a yellow solid which was sublimed (100°, 0.10 mm) to afford 18.553 g (92%) of white, crystalline α-naphthylmethanol, mp 56–58° (lit.[35] mp 59.5–60°).

The third portion of the phenylacetyl chloride solution (above) was added to a pyridine solution of 7.830 g (0.049 mol) of the α-naphthylmethanol. Work-up as before gave 5.540 g (41%) of the crude ester as a yellow oil, bp 198–206° (0.5 mm) [lit.[36] bp 212° (4–5 mm)].

B. Photochemical Studies. Irradiation of γ-Phenyl-γ-butyrolactone (4).—The lactone **4** (3.199 g, 0.020 mol) was dissolved in 60 ml of dioxane, and the solution was divided among four quartz photolysis tubes. After degassing for 30 min, the samples were irradiated in the merry-go-round with 15 RPR-2537 Å lamps. Vpc analysis (program: 100°, 4 min, 15°/min at 270°, 4 min) showed one major and several minor products; after 380 min, no increase in product concentration was observed although **4** continued to disappear. The major product was isolated by preparative vpc (5 ft × 0.375 in. 30% UC W-98 column, 110°) and showed ir and mass spectra identical with those of an authentic sample of phenylcyclopropane (**5**) prepared by the method of Peterson and Skell.[10]

Comparative Photolysis of α-, β-, and γ-Phenyl-γ-butyrolactones (6, 7, and 4).—Photolysis tubes were prepared, containing 74 mg of α-phenyl lactone **6**, 62 mg of β isomer **7**, and 87 mg of γ-phenyl lactone **4**, respectively, dissolved in 15 ml of spectrograde acetone. A fourth sample (acetone only) served as blank. The four samples were degassed, connected to limewater bubblers to detect CO_2 evolution,[37] and irradiated with 16 RPR-2537 Å lamps. After 300 min, only the γ-phenyl lactone showed a positive CO_2 test.

Photolysis of α-Cyano-γ-phenyl-γ-butyrolactone (8).—Lactone **8** (267 mg, 1.43 mmol) was dissolved in 100 ml of acetone; 15-ml aliquots were pipetted into six quartz tubes, and the samples were degassed and irradiated for 6 hr in the merry-go-round (16 RPR-2537 Å lamps). Vpc analysis as above showed two major products. Evaporation of the solvent gave 200 mg of material which was chromatographed on a 2.5 × 56 cm column of Davison Grade 950 silica gel, slurry packed with 5% ether–hexane, to afford (200-ml fractions) fractions 1–8, 5% ether–hexane eluent, nil; 9–14, 5% ether–hexane, 89 mg (48%) of *trans*-2-phenylcyclopropanecarbonitrile (**10**); 15–20, 5% ether–hexane, nil; 21–23, 50% ether–hexane, 80 mg (44%) of the cis isomer **9**.

The crude **10** from fractions 9–14 was further purified by chromatography on a 1.2 × 28 cm Florisil column, preparative tlc on silica gel (10% ethyl acetate–benzene eluent), and sublimation (90°, 40 mm) to give white crystals, mp 50.5–51.5°, mmp 49–51°, having nmr and ir spectra identical with those of an authentic sample (*vide supra*).

Anal. Calcd for $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.78. Found: C, 84.01; H, 6.53; N, 9.74.

The crude **9** from fractions 21–23 was purified by column chromatography and preparative tlc as above, then micro distilled (80°, 35 mm) to give a water-white oil having nmr and ir spectra identical with those of an authentic sample of **9** (*vide supra*).

Anal. Calcd for $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.75; H, 6.37; N, 9.95.

Photolysis of *cis*- and *trans*-2-Phenylcyclopropanecarbonitrile (9 and 10).—The isomeric nitriles (29 mg cis, **9**; 25 mg trans, **10**) were individually photolyzed in ether solvent (quartz tubes, merry-go-round, 16 RPR-2537 Å lamps). Aliquots were analyzed by vpc (column 170°). Both isomers were found to reach the same photostationary state, 46.8% trans, 53.2% cis. Some polymerization was observed in both samples, and a new product was formed in low yield. This product was not investigated further.

Preparative Photolysis of *cis*- and *trans*-α,γ-Diphenyl-γ-butyrolactone (11 and 12).—To obtain sufficient photoproduct for isolation and identification, the synthetic mixture of lactones **11** and **12** was used without separation. The mixture of **11** and **12** (1.051 g, 4.42 mmol) was dissolved in 120 ml of methanol, and the solution was divided among eight quartz tubes, degassed, and irradiated (merry-go-round, 16 RPR-2537 Å lamps). After 180 min, the solvent was removed under vacuum to give 880 mg of material which was chromatographed on a 2.5 × 54 cm column of Davision grade 950 silica gel, slurry packed with hexane, to afford (125-ml fractions) fractions 1–8, hexane eluent, nil; 9–12, 1% ether–hexane, nil; 13–16, 2% ether–hexane, nil; 17–19, 5% ether–hexane, nil; 20–22, 5% ether–hexane, 319 mg of a mixture of photoproducts (by vpc); 23–28, 5% ether–hexane, 15 mg of residue; 29–31, 20% ether–hexane, 33 mg of residue; 32–34, 20% ether–hexane, 183 mg of trans lactone **12**; 35–36, 20% ether–hexane, 9 mg of residue; 37–42, 20% ether–hexane, 289 mg of cis lactone **11** (44% recovery of starting material).

The mixture of photoproducts from fractions 20–22 was separated by chromatography on a 1.5 × 46 cm column of 20% silver nitrate on Davison silica gel, slurry packed with hexane, 75-ml fractions, to give fractions 1–5, 0.5% ether–hexane, nil; 6–10, 1% ether–hexane, 6 mg of residue; 11–16, 1% ether–hexane, 57 mg (12%) of *trans*-1,2-diphenylcyclopropane (**14**); 17–28, 1% ether–hexane, 84 mg (18%) of *cis*-1,2-diphenylcyclopropane (**13**); 29–42, 1% ether–hexane, and 43–53, 2% ether–hexane, 101 mg (18%) of 1,3-diphenylpropyl methyl ether (**15**). The photoproducts were identified by spectral comparison with authentic samples (*vide supra*).

Preparative Photolysis of Benzyl Phenylacetate (16).—The ester **16** (4.014 g, 0.0178 mol) was dissolved in 230 ml of dioxane, degassed for 30 min, and irradiated with the medium-pressure Hanovia lamp, Vycor filter (cutoff, 240 nm). Aliquots were taken at intervals for vpc analysis (column program: 110°, 4 min, 15°/min to 270°; 4 min). After 30 min, two new peaks appeared in the vpc; after 198 min, the ratio of new peaks to reactant was 1:16:45. The solvent was removed *in vacuo* to give 3.88 g of crude material. A 1.007-g portion of the crude product mixture was chromatographed on a 1.5 × 46 cm column of Davison grade 950 silica gel, slurry packed with hexane, 75-ml fractions (analyzed by vpc as above) to afford fraction 1, hexane eluent, nil; 2–3, hexane, 234 mg of dibenzyl (**17**); 4–8, hexane, 7 mg residue; 9, 10% ether–hexane, nil; 10–13, 10% ether–

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[35] K. Zielger, *Ber.*, **54**, 737 (1921).

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hexane, 438 mg of unreacted **16**; 14–20, 10% ether–hexane, 26 mg of a complex mixture of minor products. The column was washed with 200 ml of ethyl acetate and 200 ml of methanol to give an additional 156 mg of high-polarity products.

The remainder of the photolysis mixture was chromatographed as above to provide a combined total of 1.037 g (32%) of dibenzyl (**17**), 1.784 g (44%) of unreacted **16**, and 637 mg of a complex mixture of high-polarity minor products (probably solvent-derived coupling products, by analogy with the results of Zimmerman and Sandel[7]).

Photoproduct **17** was further purified by sublimation (47°, 0.01 mm) and recrystallization from 95% ethanol, mp 52–53° (mixture melting point unchanged).[26]

Photolysis of *p*-Methylbenzyl *p*-Methoxyphenylacetate (22).—The ester **22** (1.521 g, 5.63 mmol) was dissolved in 330 ml of dioxane and the solution was degassed for 30 min and irradiated with the Hanovia medium-pressure mercury arc (Vycor filter) for 180 min. Vpc analysis (column program: 110°, 2 min; 15°/min to 270°, 6 min) showed three products in a ratio of 1:2.5:1. The solvent was removed *in vacuo* to give 1.401 g of crude product, which was chromatographed on a 2.5 × 50 cm column of Davison grade 950 silica gel, slurry packed in hexane, to provide (200-ml fractions, analyzed by vpc as above) fractions 1–6, hexane eluent, 30 mg of residue; 7–11, 1% ether–hexane, 12 mg of residue; 12–14, 2% ether–hexane, nil; 15–19, 2% ether–hexane, 517 mg of a mixture of **20** and **21**; 20–24, 2% ether–hexane, 11 mg of residue; 25–30, 2% ether–hexane, 282 mg of **23**; 41–45, 4% ether–hexane, nil; 46–53, 10% ether–hexane, 562 mg (37%) of unreacted **22**; ethyl acetate and methanol washes as above gave 217 mg of high-polarity products.

The white, crystalline di-*p*-methoxydibenzyl (**21**) from fractions 25–30 had nmr (CCl_4, TMS) δ 6.95 (m, 8 H), 3.75 (s, 6 H), 2.81 (s, 4 H); ir (CCl_4) 3.31 (sh); 3.42, 3.50 (m); 6.22, 6.63 (s); 7.70 (m); 8.05–8.35 (broad, s); 8.50, 9.70 μ (s); mass spectrum (70 eV) *m/e* (rel intensity) 242 (20), 121 (100). Sublimation (120°, 0.1 mm) gave mp 124–127° (lit.[38] mp 125–126°).

Photoproducts **20** and **23** from fractions 15–19 were isolated by preparative vpc (5 ft × 0.375 in. 30% UC W-98, 220°). The di-*p*-methyldibenzyl (**20**) was further purified by sublimation (70°, 0.1 mm): mp 78–81° (lit.[39] mp 78–80°); nmr ($CDCl_3$, TMS) δ 7.02 (s, 8 H), 2.87 (s, 4 H), 2.32 (s, 6 H); ir ($CHCl_3$) 3.22, 3.26, 3.32 (sh m); 3.40 (s); 3.48, 6.62, 6.92 (m); 9.10, 9.80 (w); 12.3–14.0 μ (broad, s); mass spectrum (70 eV) *m/e* (rel intensity) 210 (24), 105 (100). The *p*-methoxy-*p'*-methyldibenzyl (**23**) was purified by sublimation (70°, 0.1 mm): mp 61–62.5°; nmr ($CDCl_3$, TMS) δ 7.05 (s) superimposed on 6.93 (m, 8 H), 3.69 (s, 3 H), 2.82 (s, 4 H), 2.28 (s, 3 H); ir ($CHCl_3$) 3.21, 3.27, 3.32 (sh, m); 3.40, 3.48, 3.50, 6.21 (s); 6.31 (m); 6.65 (s); 6.84, 6.88 (sh, m); 6.93, 7.70, 8.05–8.33, 8.52 (s); 9.10 (m); 9.70 (s); 12.15–13.95 μ (s); mass spectrum (70 eV) *m/e* (rel intensity) 226 (14), 121 (100), 105 (11).

Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.64; H, 8.02.

Preparative photolysis of 536 mg (1.99 mmol) of **22** in isopropyl alcohol (30 ml) for 920 min with 15 RPR-2537 Å lamps gave 463 mg of material after removal of the solvent. Chromatography of the photolysate on a 1.5 × 52 cm column of Davison grade 950 silica gel (as above) afforded 223 mg of a mixture of **20** and **23**, 47 mg of **21** (total dibenzyl recovery 60%), and 21 mg (4%) of unreacted **22**. Nmr analysis indicated 58% formation of the unsymmetrical dibenzyl **23**.

Irradiation of *m*-Methylbenzyl *m*-Methoxyphenylacetate (24).—A solution of 262 mg (0.97 mmol) of **24** in 15 ml of 20% aqueous dioxane was degassed and irradiated in the merry-go-round (2537 Å). After 900 min, the solvent was removed to afford 216 mg of material which was chromatographed on a 1.5 × 50 cm column of Davison Grade 950 silica gel, slurry packed with hexane, to provide (75-ml fractions) fractions 1–5, hexane eluent, nil; 6–10, 1% ether–hexane, nil; 11–13, 2% ether–hexane, nil; 14–15, 2% ether–hexane, 95 mg of a mixture of **26** and **27**; 16–19, 2% ether–hexane, 6 mg of residue; 20–26, 5% ether–hexane, 28 mg of **28**; 27–29, 10% ether–hexane, nil; 30–33, 10% ether–hexane, 16 mg (6 mol %) of unreacted **24**. The total recovery of dibenzyl products was 60% based on unreacted starting material.

The products (**26**, **27**, and **28**) were identified spectroscopically. The di-*m*-methoxydibenzyl (**28**) from fractions 20–26 had nmr (CCl_4, TMS) δ 7.06 (m, 2 H), 6.65 (m, 6 H), 3.70 (s, 6 H), 2.84 (s, 4 H); ir (CCl_4) 3.28 (sh); 3.31 (w); 3.38 (m); 3.48, 3.51, 5.82 (w); 6.28, 6.30 (s); 6.72, 6.82, 6.88, 6.96 (w); 7.63 (sh, m); 7.95 (s); 8.40 (w); 8.60 (sh, m); 8.68 (s); 9.20 (m); 9.52 (s); 9.85 (sh, m); 11.48, 11.80 (w); 14.43 μ (m); mass spectrum (70 eV) *m/e* (rel intensity) 242 (44), 122 (21), 121 (100), 91 (48), 77 (21).

The mixture of di-*m*-methyldibenzyl (**26**) and *m*-methoxy-*m'*-methyldibenzyl (**27**) from fractions 14–15 showed nmr (CCl_4, TMS) 6.95, 6.65 (overlapping m's), 3.60 (s), 2.78 (s), and 2.25 (s). The products were separated by preparative vpc (8 ft × 0.375 in., 30% UC W-98, 200°) to obtain infrared and mass spectra of the pure product. Compound **26** had ir (CCl_4) 3.20 (sh, w); 3.30, 3.40, 3.48 (s); 5.18, 5.40, 5.63, 5.72 (w); 6.22 (s); 6.29, 6.73 (m); 6.92 (s); 7.28 (m); 7.47 (w); 7.95, 8.55 (m); 9.20, 9.75 (s); 11.17 (w); 11.38 (m); 14.39 (s) (identical with literature spectrum); mass spectrum (70 eV) *m/e* (rel intensity) 210 (14), 105 (100). Compound **27** had ir (CCl_4) 3.20 (sh, w); 3.28, 3.31 (m); 3.39 (s); 3.48, 3.51 (m); 6.24, 6.31 (s); 6.72, 6.83, 6.88, 6.96 (m); 7.25 (w); 7.93 (s); 8.40 (w); 8.50 (m); 8.68 (s); 9.20, 9.25 (w); 9.48, 9.55 (s); 10.05 (w); 11.40 (m); 11.80 (w); 14.40 (s); mass spectrum (70 eV) *m/e* (rel intensity) 226 (33), 121 (83), 105 (100).

Irradiation of *m*-Methoxybenzyl *m*-Methylphenylacetate (25).—As above, a solution of 308 mg (1.14 mmol) of **25** in 15 ml of 20% aqueous dioxane was degassed and irradiated at 2537 Å for 900 min. Removal of the solvent and chromatography as above gave fractions 14–15, 2% ether–hexane, 157 mg of di-*m*-methyldibenzyl **26** and *m*-methoxy-*m'*-methyldibenzyl **27** (nmr, ir spectra identical with those of fractions 14–15 above); 18–22, 5% ether–hexane, 34 mg of di-*m*-methoxydibenzyl (**28**) (nmr, ir spectra identical with those of fractions 20–26 above); no starting material was recovered (total 74% recovery of dibenzyl products). No photosolvolysis products[7] were detected by vpc or spectral analysis, or from column chromatography.

Irradiation in Methanol–Sodium Acetate.—As a further test of the radical character of the decarboxylation, the meta-substituted esters **24** and **25** were also irradiated in methanol saturated with sodium acetate (~1.4 *M*). Two samples were prepared in quartz tubes, containing 327 mg (1.21 mmol) of **24** and 328 mg (1.22 mmol) of **25**, respectively, in 15 ml of methanol saturated with sodium acetate. These were degassed and irradiated with 15 RPR-2537 Å lamps for 500 min. The methanol was removed *in vacuo* and 30 ml of benzene was added. After stirring for 4 hr, the benzene fraction was analyzed by vpc as above. Ester **24** showed 60% conversion to give >95% of the dibenzyl products **26**, **27**, and **28**, by vpc comparison with a standard sample of 208 mg (0.77 mmol) of **24** in 15 ml of dry dioxane. Ester **25** showed complete conversion, to give the dibenzyls (81% of volatile products) and two new major and three minor products (19%). A dark reaction was run with 263 mg of **25** in 20 ml methanol, saturated with sodium acetate, maintained at 42–43° for 420 min under nitrogen. Work-up and vpc analysis as above showed 70% conversion to two new products which had the same retention times as the major products in the photochemical run (by coinjection).

Photolysis of Allyl Phenylacetate (29).—A solution of 323 mg (1.83 mmol) of **29** in 15 ml of dioxane was degassed, attached to a linewater bubbler to detect CO_2 formation,[37] and irradiated at 2537 Å with continuous degassing. After 2020 min, the sample showed only traces of $CaCO_3$ in the bubbler; vpc analysis (column program 110°, 4 min; 20°/min to 270°, 4 min) showed four major and five minor products which were not investigated further.

Photolysis of Furfuryl Phenylacetate (30).—As above, 346 mg (1.60 mmol) of **30** was dissolved in 15 ml of dioxane, degassed, and irradiated at 2537 Å (limewater bubbler used to detect CO_2). After 15 min, the bubbler solution was opaque. At 2020 min, vpc analysis (as above) showed *ca.* 60% conversion to three products (relative areas 1:3:2). The solvent was removed and the residue (285 mg) was chromatographed on a 1.5 × 54 cm column of Davison Grade 950 silica gel, slurry packed with hexane, to give (75-ml fractions) fractions 1–5, hexane eluent, nil; 6–10, 1% ether–hexane, nil; 11–13, 2% ether–hexane, nil; 14–15, 2% ether–hexane, 52.9 mg of a mixture of bifurfuryl (**33**), 1-(2-furanyl)-2-phenylethane (**32**), and dibenzyl (**17**) (in order of increasing retention time); 16–17, 2% ether–hexane, nil; 18–20, 4% ether–hexane, nil; 21–26, 4% ether–hexane, 45

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mg (13%) of unreacted **30**. Both the ester **30** and the photoproducts **32** and **33**, appeared to decompose during chromatography.

The mixture of photoproducts **17**, **32**, and **33** from fractions 14–15 had nmr (CCl_4, TMS) δ 7.12 (broad s), 6.17 (d of d), 5.88 (s), 5.83 (s), 2.90 (s), 2.87 (s); ir (CCl_4) 3.22 (sh): 3.25 (m); 3.28, 3.37, 3.40 (s); 3.48 (m); 5.78 (w); 6.27 (m); 6.70, 6.90, 7.95, 8.03, 8.72, 9.30, 9.73, 9.90, 11.63, 14.40 μ (s). Mass spectra (70 eV) of the products were obtained with the gc/mass spectral interface. **33** had *m/e* (rel intensity) 162 (23), 81 (100), 53 (22); **32**, 172 (25), 91 (31), 81 (100), 65 (9), 53 (12); **17**, 182 (19), 91 (100), 65 (13).

Photolysis of α-Naphthylmethyl Phenylacetate (31).—As above, the irradiation of the ester was monitored by use of a limewater bubbler; 336 mg (1.22 mmol) of **31** in 15 ml of dioxane was degassed and irradiated (2537 Å). After 2900 min, vpc analysis (as above) showed three products (relative areas 1:10:1) in *ca.* 40% yield; limewater test was positive. Removal of the solvent and chromatography of the residue (327 mg) on a 1.5 × 52 cm column of Davison Grade 950 silica gel, slurry packed with hexane, gave (75 ml fractions) 1–6, hexane eluent, 3 mg residue; 7–10, 1% ether–hexane, 2 mg residue; 11–13, 2% ether–hexane, nil; 14–16, 2% ether–hexane, 114 mg (40%) of a mixture of dibenzyl (**17**), 5%, and 1-α-naphthyl-2-phenylethane (**34**), 95%; 17–18, 2% ether–hexane, 3 mg of residue; 19–22, 4% ether–hexane, nil; 23–27, 10% ether–hexane, 130 mg (39%) of unchanged **31**. The di-α-naphthylethane was present in only trace quantities. However, it was shown to be present by coinjection with a sample obtained from the RPR 3000 Å irradiation (*vide infra*).

The viscous oil from fractions 14–16 had nmr ($CDCl_3$, TMS) δ 7.22 (s) superimposed on 8.20–7.13 (m, 12 H), 3.18 (AA′BB′, 4 H); ir ($CHCl_3$) 3.25, 3.31, 3.39 (s); 3.48 (m); 5.15, 5.37, 5.55 (w); 6.26, 6.70, 6.90, 7.20 (m); 8.60 (w); 9.30, 9.72, 9.85 (m); 10.38, 11.68 (w); 14.45 μ (s); mass spectra (70 eV, gc/mass spectral interface) **17**, *m/e* (rel intensity) 182 (12), 92 (9), 91 (100), 65 (15) (identical with authentic mass spectrum of dibenzyl); **34**, 232 (19), 142 (12), 141 (100), 115 (16), 91 (6).

Photolysis of **31** with the RPR-3000 Å lamps (568 mg **31**, 2.06 mmol, in 15 ml dioxane) led to a positive limewater test. Vpc analysis showed 54% conversion after 2850 min, with three products formed in a 1:13:1 ratio. The major product was identical with 1-α-naphthyl-2-phenylethane (**34**) by vpc coinjection. Dibenzyl (**17**) was also observed as a minor product. Removal of the solvent and addition of ether resulted in formation of white crystals of 1,2-di-α-naphthylethane (**35**), mp 161–163° (lit.[40] mp 161–162°).

Solvent Effects on the Photostationary State of *cis*- and *trans*-1,2-Diphenylcyclopropane.—Samples of synthetic *cis*- and *trans*-1,2-diphenylcyclopropane (**13** and **14**) were dissolved in 15 ml of solvent, degassed, and irradiated in the merry-go-round at 2537 Å. Aliquots were withdrawn at intervals for vpc analysis (column 200°). For each solvent, the photostationary state was reached from *ca.* 5% excess cis or from 5% excess trans. The results are summarized in Tables III and IV.

Quantum Yield Determinations. General Procedure.—A solution of the lactone or ester in 15 ml of solvent in a quartz tube was degassed, placed in the merry-go-round, and irradiated with the RPR-2537 Å lamps. Light output was monitored by potassium ferrioxalate actinometry by the method of Hatchard and Parker.[41] Samples were withdrawn at intervals and analyzed directly by vpc.

Quantum yields for carbon dioxide evolution were measured by passing oxygen-free dry nitrogen through the photolysis mixture. The effluent gas from the photolysis vessel was then passed through a tared Ascarite–Anhydrone (magnesium perchlorate) trap.

Registry No.—**4**, 1008-76-0; **8**, 33574-07-1; **9**, 5279-82-3; **10**, 5590-14-7; **11**, 20272-24-6; **12**, 20272-26-8; **16**, 102-16-9; **18**, 36707-18-3; **19**, 33574-08-2; **20**, 538-39-6; **21**, 16557-55-2; **22**, 33574-09-3; **23**, 36707-23-0; **24**, 36707-24-1; **25**, 36707-25-2; **26**, 4960-53-6; **28**, 36707-27-4; **30**, 36707-28-5; **31**, 36707-29-6; **32**, 36707-30-9; **33**, 36707-31-0; **34**, 36707-32-1.

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Kinetic Control in the Formation of Dienamines. Cross-Conjugated Dienamines of $\Delta^{3(9)}$-4-Hydrindenones

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A series of $\Delta^{3(9)}$-4-hydrindenones gives, with pyrrolidine, pure cross-conjugated dienamines. Systematic attempts to demonstrate the presence or to prepare the isomeric linearly conjugated dienamines having the amine group at the terminus of the diene were unsuccessful. Since the stereoisomeric 2,3-dimethyl-$\Delta^{3(9)}$-4-hydrindenones (**11**) give the corresponding cross-conjugated dienamines without any interconversion, this is regarded as a direct evidence for kinetic control in the formation of these bicyclic dienamines as a group. This generalization is supported by synthesis of the dienamines with N-deuterated pyrrolidine. The high regiospecificity of the reaction is explained in terms of steric hindrance in the concerned bicyclic system.

The enamines of 2-methylcyclohexanone and related unsymetrical ketones are known to be generally formed by thermodynamic control process. The less-substituted olefin is formed by a fast equilibrium, with steric effect control.[1,2]

The formation of the dienamines of α,β-unsaturated ketones also seems to be thermodynamically controlled, but products generally appear as mixtures of several dienamines, among which linear forms are predominant or exclusive. The yields in cross-conjugated forms are dependent on the structure of the reacting ketone and, for each ketone, on the structure of the antagonist secondary amine.[3,4] The determining factors for the ratio between linear and cross-conjugated dienamines are steric effects.[5] However,

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