Photodecarboxylation. A Labeling Study. Mechanistic Studies in Photochemistry. 15[1]

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Abstract: The photodecarboxylation of a series of benzyl and naphthylmethyl phenylacetates (**1**, **2**, **3**, and **4**) and 3,5-diphenyl-γ-butyrolactones (**5** and **6**) was examined in detail by three labeling studies. Cage effects on the product forming step from 2-naphthylmethyl phenylacetate (**3**) were readily established by deuterium labeling studies as well as by low temperature irradiations. The calculated cage combination ratio for product distribution and for deuterium label distribution provide evidence for coupling of the generated arylmethyl radicals in a manner dictated by ordinary diffusion-controlled processes. The scrambling of the carboxy oxygen atoms was shown to occur very efficiently for the 1- and 2-naphthylmethyl phenylacetates ($\Phi_2^{\text{scramble}} = 0.04$ and $\Phi_3^{\text{scramble}} = 0.16$); in fact, this was found to be the most efficient reaction for these esters. Less efficiently, benzyl phenylacetate (**1**, $\Phi_1^{\text{scramble}} = 0.02$) and 1-phenylethyl phenylacetate (**4**) undergo the same scrambling process. Optically active 1-phenylethyl phenylacetate did not racemize with extended irradiation, providing evidence for a stereospecific oxygen interchange. Irradiation did not interconvert *cis*- and *trans*-α,γ-diphenyl-γ-butyrolactones (**5** and **6**) nor scramble a carbonyl-^{18}O labeled sample of **5**, indicating that ^{18}O scrambling occurs in the flexible esters capable of a one-step ${}_{\pi}2_s + {}_{\sigma}2_s$ migration, a transformation unavailable to the lactones.

Among the known photochemical processes of esters the expulsion of carbon dioxide is one of the most important.[3] This reaction is particularly noteworthy when the carboxyl group is one atom removed from a chromophoric radical-stabilizing function, e.g., phenyl, furanyl, etc.[3,4] Our studies on photodecarboxylations of benzyl and naphthylmethyl esters **1–3** have shown that this reaction is quite general, but that, in fact, it is a low quantum efficiency reaction.[5] This low efficiency was puzzling in view of the highly efficient loss of carbon monoxide and sulfur dioxide from very similar compounds like dibenzyl ketone[6] and dibenzyl sulfone.[7]

In order to investigate the origin of the inefficiency of the decarboxylation reaction three types of labeling studies were initiated: (1) a deuterium label was introduced on the methylene groups of **3** to establish the nature of the radical coupling process after loss of carbon dioxide.[8a] (2) Oxygen-18 was introduced into the ether oxygen for **1–3** as well as **4** and for the carbonyl oxygen of lactone **5** in order to test the positional integrity of the carboxyl oxygens on irradiation. (3) Finally, the ether carbon–oxygen bond stereochemistry was investigated for ester **4** and reinvestigated for lactones **5** and **6**.[4] Here, the structural features of the lactone ring limit the available pathways for oxygen interchange, while the chiral ester **4** provides a stereochemical probe for that process.

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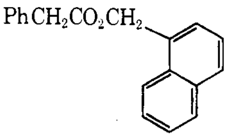

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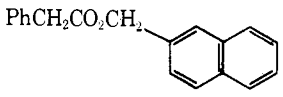

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$PhCH_2CO_2\overset{*}{C}HCH_3Ph$

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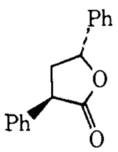

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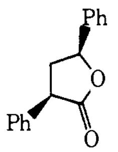

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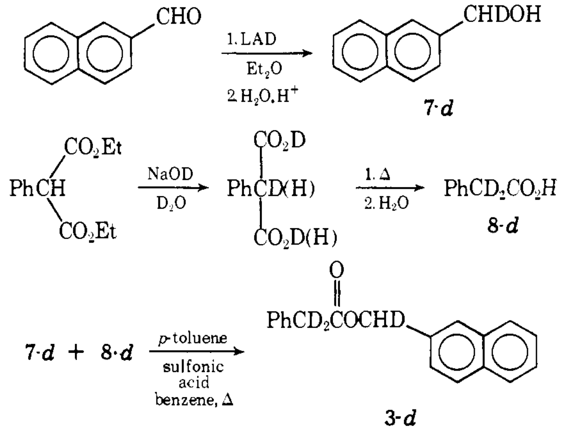
Results

Deuterium Label Studies. Synthesis of the deuterium-labeled ester is outlined in Scheme I. Deuterium labeling was accomplished by reduction of 2-naphthaldehyde with lithium aluminum deuteride giving 2-naphthylmethanol-*1′-d* (**7-*d***). The exchange and hydrolysis of diethyl phenylmalonate with basic deuterium oxide followed by pyrolytic decarboxylation gave labeled phenylacetic acid (**8-*d***). Acid-catalyzed esterification of **7-*d*** and **8-*d*** gave labeled 2-naphthylmethyl phenylacetate (**3-*d***).

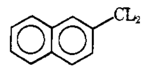
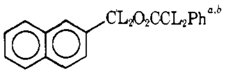
Scheme I. Synthetic Route to 1′-Deuterio-2-naphthylmethyl Deuteriophenylacetate (3-*d*)



Irradiation at 300 nm of a 1:1 mixture of **3-*d*** and **3-*h***[8b] for 6 h converted 50% of the ester to products. Isolation of the unreacted ester mixture and the major product, 1-(2-naphthyl)-2-phenylethane (**9**), was accomplished by GLC. Mass spectral analysis of an unirradiated sample and recovered sample of the ester indicated no significant isotopic fractionation during the photolysis. Mass spectral analysis of the decarboxylation product **9** is given in Table II. The deuterium distributions were determined according to the standard method of Biemann[9] and are reported as percent deuterium for **3-*d*** and for **9**. Predicted values for cage and noncage combinations are also given in Table II based on the fragment percentages in Table I.

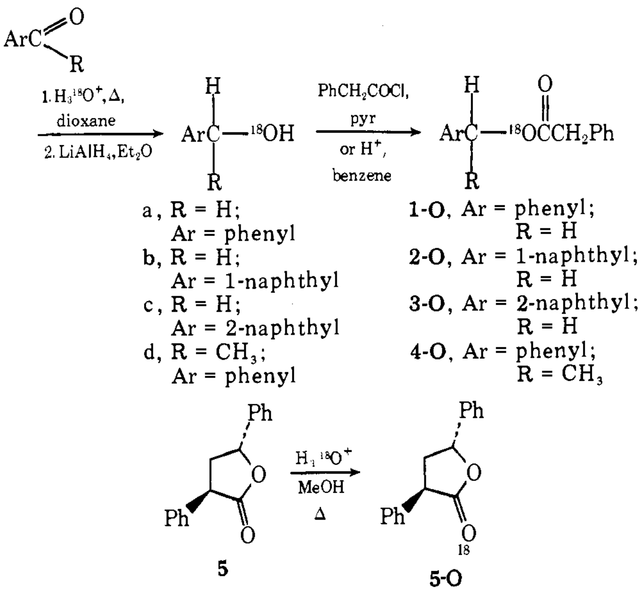
As an added test for the cage recombination step, 2-naphthylmethyl phenylacetate (**3**) was irradiated in a frozen benzene glass (dry ice temperature). After several hours ir-

Table I. Deuterium Distribution for Labeled Fragments 7-*d*, 8-*d*, and 2-Naphthylmethyl Phenylacetate (3-*d*)

	 CL_2OH^a **7-d**	$PhCL_2CO_2H^a$ **8-d**	 $CL_2O_2CCL_2Ph^{a,b}$ **3-d**
d_0	4.4	18.7	4.4
d_1	95.6	35.4	15.3
d_2	0	46.4	35.8
d_3	0	0	44.4

[a] L = H or D. The deuterium distribution was determined according to the method of Biemann.[9] The values are averages of three or more measurements with an error of 2%. [b] Values for the ester were the same (within experimental limits) both before and after irradiation to 50% conversion.

Scheme II. Synthesis of Oxygen-18 Labeled Esters 1–4 and Lactone 5



radiation, the sample was analyzed by GLC. The ratio of the three products, hydrocarbons **10**, **9**, and **11** (Ar = 2-naphthyl, Ar′ = phenyl, R = H (see Discussion and Scheme III)), was 1:30:1 indicating a cage/noncage ratio of 8:1, significantly higher than the 2:1 value found in benzene at 40 °C.

Oxygen-18 Labeled Ester. The incorporation of oxygen-18 was carried out for five compounds, benzyl phenylacetate (**1**), 1- and 2-naphthyl phenylacetate (**2** and **3**), 1-phenylethyl benzylacetate (**4**) and *trans*-2,5-diphenyl-5-hydroxybutanoic acid lactone (**5**). For esters **1-*O*** though **4-*O***[8b] oxygen-18 incorporation consisted of $H_2{}^{18}O$ acid-catalyzed exchange of the aldehyde or ketone precursor to the alcohol moiety (Scheme II). The carbonyl derivatives were reduced with lithium aluminum hydride then converted to the ester by reaction with phenylacetyl chloride in pyridine or by acid-catalyzed esterification with phenylacetic acid. For the diphenyl lactone **5-*O***, the exchange was carried out directly on the lactone introducing oxygen-18 into the carbonyl group.

Mass spectral analyses of the esters before and after irradiation showed that the ^{18}O content remained constant. Analysis for the position of oxygen-18 (ether or carbonyl oxygen) was performed on the lithium aluminum hydride reduction products (2-phenylethanol and ArCRCHOH) and are given in Table III.

The 1- and 2-naphthylmethyl esters **2-*O*** and **3-*O*** were studied at various conversions and a value for the quantum efficiency of the scrambling process was estimated. These values were then added to the previously determined decarboxylation quantum efficiencies to give an estimate of the overall C–O bond breaking efficiency as a function of the structure of the ester. Values of the scrambling efficiency and the total efficiency are listed in Table III.

Stereochemical Probes. In the third series of experiments, (*S*)-(−)-1-phenylethyl phenylacetate ((*S*)-(−)-**4**) was irradiated to 61% conversion. The ester was recovered and the specific rotation measured. The values obtained (Table IV) were the same within experimental error as those measured before irradiation, indicating no racemization at the chiral center during the irradiation. In an additional study on the stereochemical integrity of the *trans*- and *cis*-2,5-diphenyl-5-hydroxybutanoic acid lactones, **5** and **6** were found not to interconvert on direct irradiation.[4]

In an attempt to generate the benzyl and phenylacetate intermediates (A, Scheme III) by an independent route, the thermal decomposition of corresponding-*N*-nitroso-*N*-substituted phenylacetamides[11] was examined. *N*-Benzyl- and *N*-(1-phenylethyl)phenylacetamide (**12** and **13**) were treated with dinitrogen tetroxide in CCl_4, according to the method of White,[12] to yield the yellow-green *N*-nitrosoamides **14** and **15**, respectively. Thermal decomposition of the nitrosoamide in refluxing benzene or hexane gave the corresponding esters. For *N*-nitroso-*N*-benzylphenylacetamide (**14**), only benzyl phenylacetate (**1**) was obtained in >90% yield. No decarboxylation occurred as evidenced by the absence of dibenzyl and toluene. For *N*-nitroso-*N*-(1-phenylethyl)phenylacetamide (**15**), 1-phenylethyl phenylacetate (**4**) accounted for 55–60% of the product and phenylacetic acid for the remainder (see Table V). No decarboxylation occurred.

Discussion

The study of this series of labeled esters has aided significantly in the delineation of the chemical and photochemical processes which occur when arylmethyl esters are irradiated. Earlier[5] we suggested a mechanistic scheme for the 2-naphthylmethyl phenylacetate photochemistry, which has

Table II. Experimental and Estimated Deuterium Distribution in 1-(2-Naphthylmethyl)-2-phenylethane (**9**)

	Exptl from irradiation[a] of		Estimated[b]		
	3-*d*	1:1 **3-*d*/3-*h***	100% cage	70% cage, 30% noncage	100% noncage
d_0	2.6 ± 0.3	47.3 ± 1.3	51.8 ± 0.3	45.9 ± 1.4	32 ± 4
d_1	17.8 ± 0.3	16.8 ± 1.0	8.9 ± 0.3	18.0 ± 1.4	37 ± 4
d_2	37.2 ± 0.7	18.2 ± 0.3	18.6 ± 0.7	18.3 ± 1.1	21 ± 2
d_3	42.4 ± 0.8	16.0 ± 1.6	21.2 ± 0.8	18.5 ± 0.9	11 ± 1

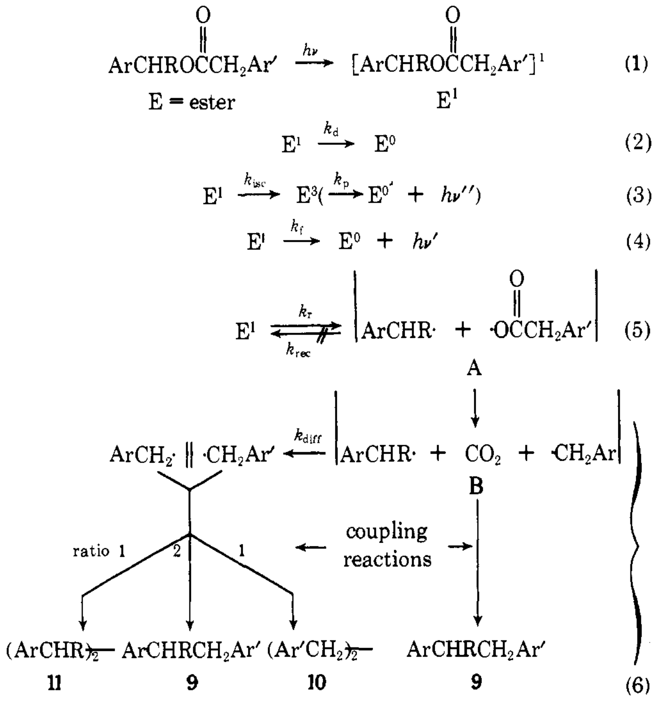
[a] Values were obtained by averaging the results of two irradiations each of which was analyzed mass spectrometrically at least two times. Irradiations were carried out under the same conditions used in preparative studies.[5] Distributions were calculated according to the method of Biemann.[9] [b] Estimated values were based on the irradiation of the deuterated ester alone (100% cage) and on the fragment deuterium distribution (100% noncage). See Table I and the Results section.

Table III. Oxygen-18 Distribution before and after Irradiation of Esters **1-*O*–4-*O*** and Lactone **5-*O***

Ester	Time, h	Irradiation,[a] % conversion	^{18}O distribution[b] C=O	^{18}O distribution[b] C-O-C	Calcd % scrambling[c] from C-O-C	Calcd % scrambling[c] from C=O	Φ_e scrambling quantum yield[d]	Φ_T total quantum yield
1		0	0.20 ± 0.02	9.83 ± 1.30				
	1.7	70	*e*	7.33 ± 1.24	52	*e*		
	3.7	75	*e*	7.34 ± 0.88	52	*e*	0.02	0.05
3		0	0.199 ± 0.028	3.485 ± 0.248			(0.16)[g]	
	6	12	0.596 ± 0.044	2.881 ± 0.162	37	24	0.14	
	10	25	0.863 ± 0.052	2.720 ± 0.104	46	40	0.10	
		0	0.20 ± 0.03	5.19 ± 0.23				
	17	47	(1.36 ± 0.07)[g]	3.42 ± 0.22	71	(46)[h]	0.08	0.22
2		0	0.195 ± 0.020	2.005 ± 0.142			(0.04)[g]	
	6	1.8	0.289 ± 0.020	1.937 ± 0.117	7	9	0.03	
	10	3	0.358 ± 0.09	1.685 ± 0.089	35	17	0.05	
	17	5	0.426 ± 0.014	1.657 ± 0.193	38	25	0.04	0.05
4		0	0.238 ± 0.028	5.868 ± 0.206				
	2.5	50	*e*	4.880 ± 0.189	35	*e*	*f*	*f*
5		0	2.28 ± 0.23[i]	0.20 ± 0.02[i]				
	1.3	53	2.16 ± 0.32	0.20 ± 0.02	0	0	0	0.03[j]

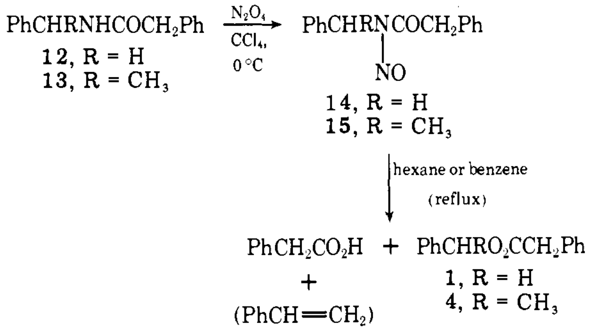
[a] Benzyl esters were irradiated in dioxane at 253.7 nm; naphthylmethyl esters in benzene at 300 nm; lactone **5-*O*** in methanol at 253.7 nm. Solutions of ca. 10^{-2} M were degassed with N_2 and irradiated in a merry-go-round apparatus[21] and were run in duplicate. [b] Calculated from the mass spectral determination (minimum of two runs, three scans each; Varian CH5 mass spectrometer) of the $(P + 2)/P$ ratio and assuming a natural abundance of ^{18}O for the 2-phenylethanol (preirradiation). Measurements were performed on the alcohols isolated from the $LiAlH_4$ reduction of the esters. [c] Calculated from the change in the ^{18}O percent of the alcohols after irradiation. [d] As determined from eq 7 using ϕ's from ref 4 and 5. [e] Experimental error range too large for reliable percentage calculations. [f] Not determined. [g] Extrapolated to zero conversion. [h] Only one determination, three mass spectral scans. [i] Calculated from mass spectral determination of $(P + 2)/P$ ratio before and after acid-catalyzed equilibration with H_2O (^{16}O). [j] 10% MeOH-ether.

Scheme III. General Mechanism of Arylmethyl Ester Photochemistry



developed into essentially a general picture for all esters studied by us and has already had more far reaching application.[13] An adaptation of that original mechanism is given in Scheme III.

In previous studies we have shown that these esters decarboxylate from the singlet manifold[4,5] (step 5, Scheme III). Although both phosphorescence and fluorescence emissions are observed (hence, steps 3 and 4), the quenching and sensitization studies in the naphthyl series showed that only the singlet state was reactive. In that same study, a pronounced solvent cage effect was indicated from the ratio of the hydrocarbon products **9–11** formed in step 6. The decay step (2) was introduced to account for the fact that the quantum yields for all measurable processes did not total unity.[14]



It is clear from the deuterium labeling studies and the low-temperature irradiation that the product composition is determined primarily from the diffusion-controlled parameters of the solvent, the temperature, and the structural makeup of the generated radicals. For the larger, less mobile naphthylmethyl radicals, the cage effects are pronounced. By choosing ester **2** or **3** and photolyzing in a benzene glass, the product yield for the cage recombination is very high, 87% of the substituted ethane product.

The oxygen labeling study has revealed a side reaction which would otherwise have gone unseen. It is interesting that oxygen scrambling, i.e., the ether, carbonyl-oxygen atom interchange, should occur in these esters. A priori it would not be expected to arise from recombination of the caged radical pair (A, Scheme III) because of the expected low barrier to decarboxylation, giving CO_2 and radical pair **B**. Furthermore, we have evidence from earlier studies that cis–trans isomerization did not accompany photodecarboxylation of lactones **5** and **6**. If an intermediate, such as carboxyl-alkyl diradical C, were involved, then recombination to scramble the oxygen functions would be observable. In addition, the common intermediate

Table IV. Specific Rotations ($[\alpha]^{35}_{\lambda}$) for (*S*)-(−)-1-Phenylethyl Phenylacetate (**4**) before and after Photolysis

	Concn,[a] g/100 mL	$-[\alpha]^{35}_{\lambda}$, nm, at λ = 589	546	436	365
Ester					
Before irradiation					
Sample 1	0.127	57.4	67.8	122.6	207.4
Sample 2	0.182	56.7	67.1	121.0	202.4
After irradiation[b]					
Sample 1a	0.102	57.9	66.8	120.0	202.3
b	0.193	58.1	68.5	121.4	203.4
Sample 2a	0.118	55.0	63.0	114.2	192.1
b	0.145	55.7	63.9	116.2	195.3
Hydrocarbon product mixture[c]					
Sample 1a	0.073	6.9	2.7	11.0	23.4
b	0.069	6.5	2.9	10.1	23.2
Sample 2	0.164	7.3	7.3	14.4	28.1

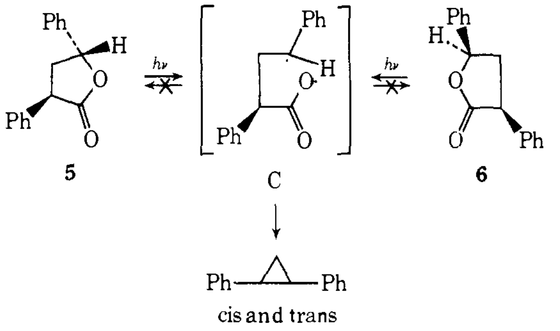
[a] 95% ethanol. [b] Irradiations were carried out in dioxane at 253.7 nm to 61% conversion. The photolysis mixture was chromatographed and the isolated pure ester and hydrocarbon mixture were examined. [c] There are no reported values for the specific rotations of enantiomeric 1,2-diphenylpropane. For 2,3-diphenylbutane the reported value is $[\alpha]^{19}_{589}$ −4.6 in ligroin.[10]

Table V. Chemical and Optical Yields from the Thermal Decomposition of Substituted *N*-Nitrosophenylacetamides **14** and **15**

Nitroso amide[a]	Run	Yields,[b] % Phenylacetic acid	Phenylacetate ester, (optical purity)[c]
N-Nitroso-*N*-benzylphenylacetamide (**14**)	1	0	**1**, 100%
	2	0	**1**, 100%
N-Nitroso-*N*-(1-phenylethyl) phenylacetamide[d] (**15**)	1	55	**4**, 45 (41.6 ± 1.3%)
	2	58	**4**, 42 (41.6 ± 1.3%)

[a] The nitrosoamides were made from the corresponding phenylacetamides by the method of White.[12] Each amide was thermally decomposed in refluxing benzene (see Experimental Section). [b] Yields are based on NMR analysis of the product mixture and on the weight of phenylacetic acid isolated from aqueous bicarbonate extraction. The styrene from **15** was not isolated. [c] Optical purities are based on the specific rotations (two measurements) at 589, 578, 546, and 486 nm and compared with optically pure **4** (Table IV). [d] The 100% optically pure amide was synthesized from optically pure (+)-1-phenylethylamine.

C should have provided the same ratio of products regardless of the identity of the lactone. In fact, neither of these were found.



However, examination of the results from the oxygen-18 studies of esters **1–4** does show that the oxygen-18 is scrambled between the ether and carbonyl oxygens very efficiently. The quantum efficiency for this exchange was calculated from the ratio of the scrambling efficiency to the disappearance efficiency:

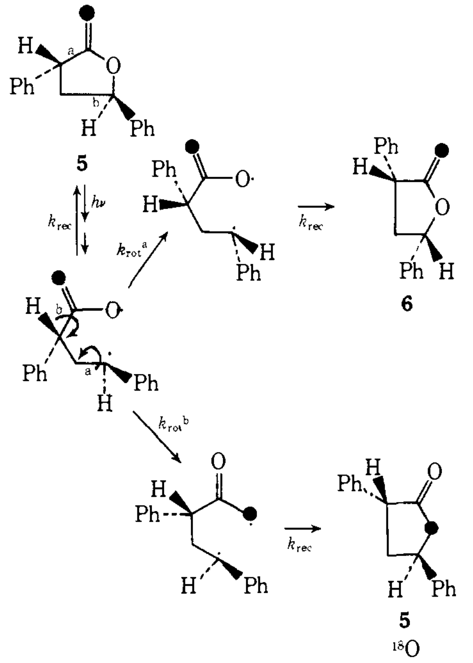
$$\%\ \text{scrambling}/\%\ \text{conversion} = \Phi_c/\Phi_{dis} \qquad (7)$$

where Φ_c and Φ_{dis} are the quantum yields for exchange scrambling and disappearance, respectively. For esters **1-3**, where quantum yields for scrambling were measured, *the efficiency of the scrambling reaction is equal to or greater than the efficiency for decarboxylation.*

In a recent, thorough study of the photochemistry of 3,5-dimethoxybenzyl acetate in aqueous methanol and aqueous dioxane, Jaeger[3b] has independently shown that oxygen-18 scrambling occurs in the photosolvolysis of **12** to 3,5-dimethoxybenzyl methyl ether and 3,5-dimethoxybenzyl alcohol. Using his values of 68 ± 4% scrambling at 52.6% conversion and Zimmerman's value for the product appearance quantum yield,[15a,b] the scrambling efficiency can be estimated to be 0.16 (0.20).[15c] This value is in surprisingly good agreement with our findings and implies that the photoreactions are very similar in nature in spite of the difference in product composition. We will comment on this point later.

In contrast to the efficient oxygen scrambling for esters, the study of lactone **5** revealed no oxygen equilibration. Diphenyllactone **5** containing 11% excess oxygen-18 in the carbonyl was irradiated to 50% conversion, reisolated, and oxygen-18 content and position analyzed. The lack of scrambling would tend to rule out the cleavage and subsequent recombination of the ether–oxygen bond via an intermediate like C, in agreement with our earlier stereochemical analysis for these lactones.[16] Although Jaeger has suggested that recombination of radical or ion pairs is the likely mechanism for oxygen scrambling, our studies would suggest that the diradicals generated form the lactones **5** and **6** do not follow this route. If the diradical does recombine, then the rate of recombination (k_{rec}) must exceed the rate of rotation about either bond (k_{rot}^{a} and k_{rot}^{b}) by at least a factor of 10, since neither ^{18}O exchange nor cis–trans isomerization are observed (Scheme IV). (This

Scheme IV



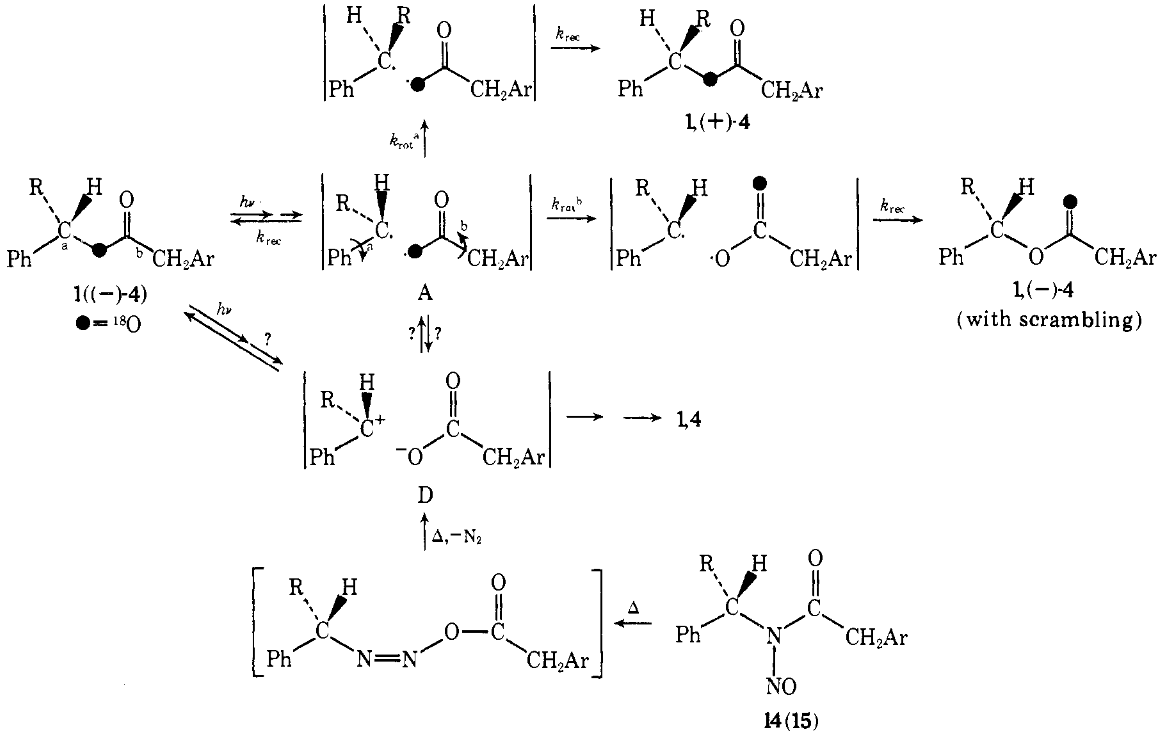
● = ^{18}O

k_{rot} = rotation rate constant

k_{rec} = recombination rate constant

(^{18}O with exchanged)

Scheme V. The Radical Pair–Ion Pair Mechanism for Oxygen and Stereochemical Scrambling of 1–4



latter observation was noted by us earlier and reconfirmed in our more recent studies (see Experimental Section)). Instead, intermediate **16** must decarboxylate faster than rotation about either bond a or b, implying that the activation energy for that process is very low, lower than the barrier to rotation a or b and recombination.

The decarboxylation step probably does not occur by simultaneous cleavage of both lactone–benzyl bonds. An analogous process, where the simultaneous cleavage of bonds that leads to a 1,3-diphenyltrimethylene diradical, has been proposed for the decomposition of *cis*- and *trans*-3,5-diphenyl-1-pyrazolines.[17] The ratios of *cis*- and *trans*-diphenylcyclopropanes generated are not in accord with our earlier findings,[4] suggesting that the initially generated diradicals from **5** and **6** undergo some rotation prior to CO_2 loss.

Extending this mechanism to the open chain esters, e.g., **1–4**, Scheme V, may not be valid, for $k_{\rm rec}$ could be much larger than $k_{\rm rot}$ for the cyclic systems, but not so for the two discreet radicals generated from the phenylacetate esters. However, two experimental observations favor a unified mechanism for the esters and lactones. The first is the complete retention of stereochemical integrity of the benzyl-carbon oxygen bond during the scrambling process. *Ester 4 remained optically pure at 61% disappearance of the ester* (75% conversion, if a 35% scrambling is included). Thus it is unlikely that the radical pair hypothesis can accommodate such a high retention of stereochemical integrity with scrambling, for $k_{\rm rot}^{\rm a}$ and $k_{\rm rot}^{\rm b}$ from A (Schemes III and V) should have similar values.

Finally, the interconversion of diradical–ion pair intermediates A ⇆ D (Scheme V) presents another potential route for benzyl esters. "Ionic" products are observed by Jaeger[3b] and Zimmerman,[16] but not found in our reactions, suggesting that D is not formed or that such an equilibrium strongly favors A. In order to test for such a possibility in our reaction, we have attempted to generate the A,D intermediate pair by a thermal decomposition of the appropriate *N*-nitrosoamides. White[11,12,18] has shown in an elegant series of investigations that ion pairs generated by the thermal expulsion of nitrogen from *N*-nitrosoamides recombine to yield esters. Tracer studies have shown that the oxygen atoms are extensively equilibrated. However, optically active 1-phenylethylamides gave the 1-phenylethyl esters with substantial retention of configuration (44–51%). Solvent effects and trapping experiments all indicated that an ion pair mechanism obtains.[18]

We[1,4,5] and others[3a,c,e] have suggested that both ion pairs and radical pairs may be important in these reactions. To enter the reaction pathway by way of an ion pair utilizing the *N*-nitrosoamides provides a modest test of this hypothesis. The separation of the two components caused by the intervening nitrogen molecule modifies (probably increases) the barrier for recombination to form the ester. However, the rotational barriers should remain unaffected.

In order to provide direct evidence relevant to the benzyl phenylacetate photochemistry, the *N*-benzyl- and (+)-*N*-(1-phenylethyl)-*N*-nitrosophenylacetamides (**14** and **15**) were thermally decomposed in refluxing benzene, producing esters **1** and **4**, respectively. The complete absence of dibenzyl from the thermolysis of **14** confirms and extends White's conclusion[18c] that radical processes are not important in this reaction.

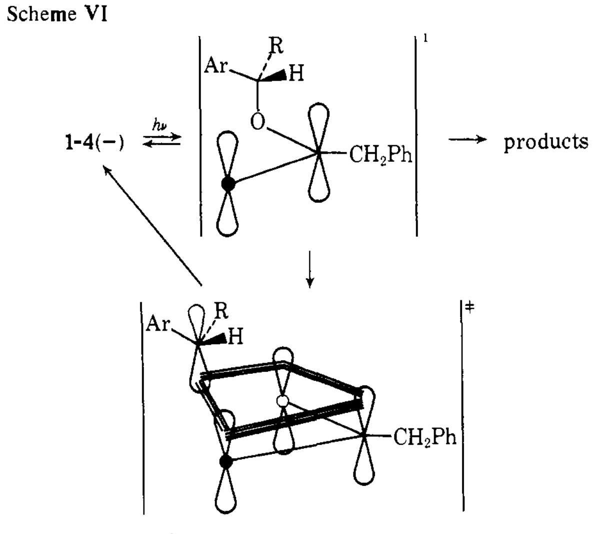
Thermolysis of **15** gave a mixture of ester **4**, phenylacetic acid, and styrene (not isolated). Again, none of the decarboxylation products were observed (NMR, GLC). The retention of configuration observed in the ester was 41%, substantially lower than our photochemical results. These results indicate that the ion pair mechanism for the photochemistry of **4** cannot account for the oxygen scrambling; otherwise the optical purity of the recovered ester would drop measureably.

We therefore suggest that ^{18}O scrambling is occurring by a 1,3-sigmatropic migration with retention of configuration of the migrating carbon, i.e., as shown in Scheme VI. Furthermore, the decarboxylation process occurs by an independent, carbon–ether oxygen cleavage step. The initially formed intermediates do not recombine, but instead go on to product. Work is in progress on other esters that should further test this hypothesis.

Experimental Section

Synthesis of Deuterium-Labeled 2-Naphthylmethyl Phenylacetate

Scheme VI



(**1-*d***). **2-Naphthylmethanol-1′-*d* (7-*d*).** Treatment of 3.504 g (22.3 mmol) of 2-naphthaldehyde with 473 mg (12.5 mmol, 2 equiv) of lithium aluminum deuteride (Biorad, 99% deuterium) gave after workup and recrystallization (ethanol–water) 3.37 g (96%) of white 2-naphthylmethanol-*1′-d* (**7-*d***): IR ($CHCl_3$) 2.77, 2.90, 3.27, 3.36, 3.39, 4.61 (C–D), 6.26, 6.65, 7.27, 7.91, 8.33, 8.58, 8.93, 9.65, 10.53, 10.64, 10.81. 11.05, 11.70, 13.89, 15.11 μm; NMR ($CDCl_3$, Me_4Si) δ 7.74–7.60 (m, 7 H), 4.72 (s, 1 H), 1.88 (s, 1 H); Mass spectrum (70 eV, 24 °C *m/e* (%)) 128 (27.3), 129 (72.7), 130 (100.0), 131 (16.4), 141 (6.9), 142 (23.6), 143 (6.0), 156 (1.1), 157 (3.3), 158 (20.0), 159 (87.3), 160 (11.3). Analysis of the deuterium content by NMR was >90% *d*. This was confirmed and more precisely estimated as 95.6% by mass spectral analysis[9] of 2-naphthylmethyl phenylacetate (**3-*d***) synthesized from **7-*d***.

2,2-Dideuteriophenylacetic Acid (8-*d*). Diethyl phenylmalonate (19.735 g, 83.5 mmol) was added dropwise to a solution of 4.354 g (0.1893 g-atom) of sodium in 30 mL of D_2O. The mixture was heated at reflux for 2 h, cooled, and poured over 10 g of ice. The solution was acidified with concentrated HCl and the malonic acid extracted with ether. Crude deuterated phenylmalonic acid obtained from the removal of the solvent was decarboxylated according to the procedure of Marvel[19] to give the crude phenylacetic acid as a yellow oil. This was dissolved in ether, extracted with 5% aqueous NaOH, and the base layer extracted with ether and acidified with concentrated HCl until the precipitation of phenylacetic acid was complete. The product was filtered washed with dilute HCl, and dried to give 4.8 g (42%) of 2,2-dideuteriophenylacetic acid as a white solid, mp 72–73 °C: IR ($CHCl_3$) 2.73, 2.85, 3.31 br, 3.76, 5.15, 5.87, 6.25, 6.70, 6.92, 7.12, 7.76, 9.33, 9.63, 9.80, 10.71, 11.91, 14.47 μ; NMR ($CDCl_3$, Me_4Si) δ 9.78 (s, 0.7 H), 7.17 (s, 5 H), 3.58 (s, 0.68 H); mass spectrum (70 eV, 16 °C, *m/e* (%)) 90 (6.2), 91 (35.7), 92 (79.8), 93 (100.0)), 94 (16.7), 95 (1.0), 135 (0.1), 136 (9.2), 137 (24.4), 138 (31.0), 139 (2.7), 140 (0.3). The mass spectrum of undeuterated phenylacetic acid was obtained under identical conditions and the relative intensities for *m/e* 135–140 were used to calculate[9] the deuterium content of **8-*d*** as 18.7% d_0, 35.4% d_1, and 46.4% d_2 (Table I).

Labeled 2-Naphthylmethyl Phenylacetate (3-*d*). A solution of 2.070 g (13.1 mmol) of labeled naphthylmethanol (**7-*d***), 1.800 g (13.1 mmol) of labeled phenylacetic acid (**8-*d***), and 280 mg of *p*-toluenesulfonic acid in 50 mL of dry benzene was heated at reflux overnight, sufficient for complete H_2O removal by azeotrope. After normal workup, 775 mg (21%) of crude red ester was obtained. The crude material was recrystallized several times from 30% ether–hexane and twice sublimed in vacuo (100–110 °C (0.01 Torr)) to give 200 mg of pure ester **3-*d*** (99% by GLC), mp 64–65.5 °C: IR (KBr pellet) 3.27, 3.29, 4.55, 5.80, 6.25, 6.69, 6.90, 7.42, 7.51, 7.69, 7.85, 7.98, 8.24, 8.50, 8.61, 8.89, 9.29, 9.54, 9.77, 10.34, 10.47, 10.88, 11.57, 11.98, 12.27, 13.51. 13.83, 14.29 μm; NMR ($CDCl_3$, Me_4Si) δ 7.60–7.19 (m, 12 H), 5.20 (s, 1 H), 3.65 (s, 0.6 H); mass spectrum (70 eV, *m/e* (%)) 90 (1.7), 91 (3.8), 92 (5.9), 93 (6.9), 94 (1.0), 95 (0.7), 140 (5.9), 141 (11.7), 142 (100.0), 143 (12.8), 144 (5.0), 145 (0.1), 275 (0.0), 276 (0.5), 277 (2.0), 278 (4.8), 279 (6.6), 280 (1.4). Analysis of the deuterium content[9] gave 4.4% d_0, 15.3% d_1, 35.8% d_2, and 44.4% d_3 (Table I).

Irradiation of Labeled and Unlabeled 2-Naphthylmethyl Phenylacetates. Samples of unlabeled ester (**3-*h***) (22.5 mg, 0.082 mmol), labeled ester (**3-*d***) (20.1 mg, 0.072 mmol), and an approximately 1:1 mixture of the esters (9.5 mg of **3-*h*** and 9.9 mg of **3-*d***) were each dissolved in 15 mL of dry benzene and placed in Pyrex tubes. After degassing with purified N_2[20] for 30 min, the samples were irradiated for 6 h (50% conversion) in a merry-go-round apparatus[21] using 15 RPR-3000 Å lamps. After evaporation of the solvent, the mixture was separated by preparative GLC. The major product (1-(2-naphthyl)-2-phenylethane, **10**) and the recovered ester were analyzed by mass spectra for the deuterium content. A second set of irradiations employing three separate samples of 21.5 mg (0.080 mmol) of **3-*h***, 20.5 mg (0.074 mmol) of **3-*d***, and a mixture of 10.2 mg (0.037 mmol) of **3-*h*** and 10.2 mg (0.037 mmol) of **3-*d*** in dioxane were analyzed each in the same manner. Both irradiations gave the same relative deuterium distribution within experimental error. The results given in Tables I and II are the average of both experiments.

Synthesis of 1- and 2-Naphthylmethanol-^{18}*O* (b and c), Benzyl Alcohol-^{18}*O* (a), and 1-Phenylethanol-^{18}*O* (d). Each alcohol was prepared by $LiAlH_4$ reduction of the labeled ketone or aldehyde.[22] The aldehydes and ketones were exchanged with $H_2{}^{18}O$ using a fourfold excess of $H_2{}^{18}O$. In a typical exchange, 1.084 (6.9 mmol) of 2-naphthaldehyde was dissolved in a mixture of 7 mL of dioxane, 0.5 mL of 30% ^{18}O-enriched water, and 0.01 mL of concentrated H_2SO_4. This solution was heated at reflux for 24 h, the solvent removed by distillation, and the remainder dissolved in 2 mL of ether. The ether solution was dried, then added dropwise to a suspension of 0.15 g of $LiAlH_4$ in 3 mL of ether. After addition was complete, the suspension was stirred for 10 h, then excess $LiAlH_4$ and the aluminum salts were hydrolyzed by addition of a saturated aqueous ammonium chloride solution. The ether layer was washed with water, dried, and evaporated in vacuo to give 0.7406 g (68%) of 2-naphthylmethanol-*1*-^{18}*O-d* (**c**). Mass spectrographic analysis gave an M/(M + 2) ratio for a 5.56% enrichment of ^{18}O in **b**. For the other alcohols, the yields and percent enrichment were: for c, 87% yield and 3.10% enrichment; for **a**, 77 and 10.45%; and for **d**, 68 and 7.69%. It was noted that the rate of ^{18}O incorporation was qualitatively fastest for benzaldehyde, then acetophenone, and slowest for the two naphthaldehydes, giving the highest enrichment in the former.

Synthesis of 1- and 2-Naphthylmethyl Phenylacetate-^{18}*O* (2-*O* and 3-*O*), Benzyl Phenylacetate-^{18}*O* (1-*O*), and 1-Phenylethyl Phenylacetate-^{18}*O* (4-*O*). The esters were prepared from the appropriate alcohols by the same method used previously[4,5] via reaction with phenylacetyl chloride and the alcohol in a benzene–pyridine solution at 0 °C. Normal workup gave the crude esters, which were purified by silica gel chromatography.

To establish the ^{18}O content of the esters, each was reduced to the two alcohols by reaction in ether with $LiAlH_4$. The mixture of the ester and $LiAlH_4$ (excess) in ether was allowed to react overnight, then cautiously hydrolyzed by addition of aqueous ammonium chloride (saturated). After hydrolysis, the ether layer was washed with water, dried ($MgSO_4$), and removed in vacuo to give a mixture of 2-phenylethanol and the enriched alcohol, **a**, **b**, **c**, or **d**. These were separated by preparative GLC (program: 100°/4 min, 20°/min to 270°/3 min; column: 0.125 in. × 6 ft, 10% UCW 98 on Chromosorb W). In each case both alcohols were analyzed for ^{18}O content mass spectrometrically[9] at 20 and 70 eV from the (P + 2)/P ratio. It was shown that the ^{18}O label was present exclusively in the alcoholic oxygen of each ester. These control reductions were carried out simultaneously with reductions of the esters recovered from photolysis. The measurements at 70 eV showed less scatter than at 20 eV and were used for all subsequent analyses.

Irradiation of Labeled Esters. The two naphthylmethyl esters were irradiated in benzene at 300 nm as described previously.[5] The two benzyl derivatives were irradiated in dioxane at 254 nm as described earlier.[4] The conversion (GLC) and ^{18}O content (mass spectrum) are given in Table III. Scrambling of ^{18}O was determined from this data and converted to quantum yields for scrambling as described in the Results section and are given in Table III.

Low Temperature Photolysis of 2-Naphthylmethyl Phenylacetate (3). Ester **3** (2.5 mg, 0.009 mmol) was dissolved in 0.4 mL of benzene in a quartz NMR tube and after degassing with purified nitrogen, the tube was placed in the quartz "Dewar" flask (Aminco-Bowmann spectrophosphorimeter attachment). The irradiation was carried out at −77 °C using a spectrograde 2-propanol and dry ice mixture as a cooling bath in a "merry-go-round" apparatus with 15 RPR-3000 Å lamps for 20 h. After photolysis the mixture was analyzed by GLC (column: UCW 98, 0.125 in. × 6 ft; program: 100°/4 min, 20°/min, 20°/min to 255°/10 min), showing 18% conversion of ester and three products: dibenzyl (**10**), 1-(2-naphthyl)-2-phenylethane (**9**), and 1,2-di-β-naphthylethane (**11**), in the molar ratio 1:30:1. The solution ratio (40 °C) of these products was 1:10:1.

Synthesis of (+)- and (−)-1-Phenylethyl Phenylacetate (4). *dl*- and *l*-1-phenylethanol[23] were treated with an excess of phenylacetyl chloride in a benzene–pyridine solution at 0 °C overnight. Normal workup[23b] followed by silica gel chromatography gave pure **4** (99% by GLC). For (±)-1-phenylethyl phenylacetate (**4**): $n^{25}{}_D = 1.5432$; IR (CCl_4) 3.28, 3.29, 3.31, 3.34, 3.39, 3.47, 5.77, 6.22, 6.57, 6.87, 7.25, 7.43, 8.00, 8.25, 6.62, 8.77, 9.37, 9.68, 9.88, 10.00, 10.44, 13.89, 14.29 μm; NMR (CCl_4, Me_4Si) δ 7.03 (s, 10 H), 5.73 (q, 1 H, $J = 6.5$ Hz), 3.47 (s, 2 H), 1.42 (d, 3 H, $J = 6.5$ Hz); mass spectrum (70 eV, *m/e* (%)) 91 (47.3), 105 (100.00), 240 (0.8).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.63; H, 6.79. For (−)-1-phenylethyl phenylacetate ((−)-**4**): from 1-phenylethanol with a specific rotation (*c*, 0.297, 95% ethanol) $[\alpha]^{35}{}_{589}$ −41.8, $[\alpha]^{35}{}_{436}$ −83.9, $[\alpha]^{35}{}_{365}$ −133.1, ester **4** was obtained with the specific rotations given in Table IV.

Photolysis of (±)-α-Methylbenzyl Phenylacetate (4). A solution of 407.0 mg (1.693 mmol) of ester **4** in 40 mL of dioxane, freshly distilled from calcium hydride, was placed in four quartz tubes, degassed 20 min with nitrogen,[20] and irradiated for 6 h in a "merry-go-round" apparatus[21] using 15 RPR-2537 Å lamps. The solvent was removed in vacuo, giving 380 mg of yellow oil which was chromatographed on silica gel. Eluting with hexane gave 84.9 mg of a mixture of hydrocarbons; with 4% ether–hexane, 79.3 mg of starting ester **4**; with 8% ether–hexane, 35.3 mg of a mixture of polar, probably solvent derived coupling products. A yellow polymeric material remained on the top of the column and was not further analyzed.

The mixture of hydrocarbons was rechromatographed on Woelm alumina (activity I); however separation of hydrocarbons was not achieved. GLC analysis showed the absence of any hydrogen abstraction products and the presence of four products with very similar retention times: a main hydrocarbon product, presumably 1,2-diphenylpropane (**9**, Ar = Ph, Ar′ = Ph, R = CH_3), and three other minor products, one of them with retention time shorter than **9**, dibenzyl (**10**, by coinjection with the known sample), and two products in the same quantities with retention time longer than **9**, presumably diastereomers of 2,3-diphenylbutane (**11**). This was confirmed by mass spectrum analysis of the mixture, showing base peak of *m/e* (relative intensity) 105 (100.0%, $PhCHCH_3^+$), 91 (H 23.8, $PhCH_2^+$), 182 (2.8, $PhCH_2CH_2Ph^+$), 196 (3.1), $PhCHCH_3CH_2Ph^+$), and 210 (0.1, $PhCHCH_3CHCH_3Ph^+$).

NMR and IR analysis of the material were also consistent with the above assignment. This material had $n^{25}{}_D = 1.556$, which is also in good agreement with reported value for **11** ($n^{25}{}_D = 1.555$ for both diastereomers).[10]

Photolysis of (−)-α-Methylbenzyl Phenylacetate ((−)-4). A solution of 81.0 mg (0.337 mmol) of (−)-**4** in 10 mL of dioxane in a quartz tube was degassed 20 min with purified nitrogen[20] and irradiated for 135 min in a "merry-go-round" apparatus[21] at 254 nm. GLC analysis showed >50% conversion of **4**. After removing of solvent 80 mg of residue was chromatographed on silica gel. Eluting with hexane gave 20.0 mg of a mixture of hydrocarbons; 2% ether–hexane, 31.5 mg (39%, 61% conversion) of the starting ester **4**; 4–8% Et_2O–hexane, 18.6 mg of mixture of polar, coupling derived solvent products (total recovery 92%). The mixture of hydrocarbons and recovered ester was analyzed polarimetrically and the results are listed in Table IV. A duplicate run using 80.0 mg (0.33 mmol) of (−)-**4** was also run and the results are also listed in Table IV.

Synthesis of Carbonyl-^{18}O Labeled *trans*-α,γ-Diphenyl-γ-butyrolactone (5-*O*). A solution of 800 mg (3.54 mmol) of the *trans*-lactone **5** was dissolved in 20 mL of methanol, 3 mL of H_2O containing 11% $H_2{}^{18}O$, and 1 mL of concentrated H_2SO_4. The mixture was heated at reflux for 5 h. The solution was cooled, and the methanol evaporated. The lactone was taken up in benzene, dried, the benzene removed in vacuo, and then recrystallized several times from methanol. The lactone was analyzed mass spectrometrically[9] for ^{18}O enrichment; the results are in Table III showing an 11.4 ± 1.2% enrichment.

Irradiation of ^{18}O Labeled *trans*-α,γ-Diphenyl-γ-butyrolactone (5-*O*). A degassed methanol (6 mL) solution of 50 mg of labeled lactone **5-*O*** was irradiated for 80 min at 254 nm as described earlier.[4] The solvent was evaporated and the residue analyzed by GLC, which indicated that there was no *cis*-α,γ-diphenyl-γ-butyrolactone (**6**) present and that the conversion of the *trans*-lactone to products was 53%. A 25-mg sample of the remaining crude mixture was dissolved in acetone (2 mL) and 2 mL of $H_2{}^{16}O$ added. The solution was heated at reflux for 16 h, cooled, and the solvent removed in vacuo. Lactone **5-*O*** was isolated by preparative GLC on a 0.125 in. × 6 ft 10% SE-30 column at 200 °C. The lactone was analyzed mass spectrometrically for ^{18}O content.[9] A control experiment with no irradiation was also carried out. These results are given in Table IV.

***N*-Nitroso-*N*-(1-phenylethyl)phenylacetamide[12] (15).** To a stirred suspension of 300 mg (1.33 mmol) of (+)-*N*-(1-phenylethyl)phenylacetamide (**13**) and 300 mg of sodium acetate in 200 mL of CCl_4 at 0 °C was added on excess of N_2O_4 (~10 min). The stirring was continued until NO_2 fumes ceased. The green solution was dried ($MgSO_4$), filtered, and the CCl_4 removed at ambient temperature (in vacuo) to give 300 mg (1.18 mmol, 88%) of *N*-nitroso-*N*-(1-phenylethyl)phenylacetamide (**15**) as an unstable green oil:[24] IR (CCl_4) 1710 (C=O), 1495 (NO) cm^{-1}; NMR ($CDCl_3$) δ 1.6 (d, 3 H, $J = 7$ Hz), 4.43 (s, 2 H), 5.95 (q, 1 H, $J = 7$ Hz), 7.33 (s, 10 H).

***N*-Nitroso-*N*-benzylphenylacetamide (14).** To a stirred suspension of 1.0 g of *N*-benzylphenylacetamide (**12**) and 0.5 g of sodium acetate in 300 mL of CCl_4 cooled to 0 °C (ice bath) was added an excess of dinitrogen tetroxide (N_2O_4) gas. After 15 min, the ice was removed and stirring continued until the brown NO_2 fumes ceased. Anhydrous magnesium sulfate was added and the green solution filtered. With removal of the solvent at ambient temperatures, a green oil was obtained. The *N*-nitroso-*N*-benzylphenylacetamide (**14**) was crystallized from hexane, mp 35–37 °C, 60 °C dec: IR (CCl_4) 1710 (C=O), 1495 (NO) cm^{-1}; NMR ($CDCl_3$) δ 4.5 (s, 2 H), 4.9 (s, 2 H), 7.3 (two s, 10 H).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 70.87; H, 5.51; N, 11.02. Found: C, 70.70; H, 5.52; N, 11.03.

Thermal Decomposition of *N*-Benzyl- and *N*-(1-Phenylethyl)-*N*-Nitrosophenylacetamides (14 and 15). A solution of ca. 300 mg of the nitrosoamide was dissolved in 50 mL of anhydrous benzene and heated at reflux for 0.5 h. The solution was cooled, extracted three times with saturated $NaHCO_3$, dried, and the solvent evaporated to give benzyl phenylacetate (**1** from **14**) or 1-phenylethyl phenylacetate (**4** from **15**), which was further purified by silica gel chromatography. The aqueous sodium bicarbonate extract was acidified to pH <3 and extracted with ether. The ether layer was dried and evaporated to give phenylacetic acid. Yields of the esters and acid and optical purities are given in Table V.

The *N*-nitrosoamides were also decomposed by refluxing in hexane for 16 h. The *N*-benzylamide gave >90% of benzyl phenylacetate (**14**) (by GLC) and no evidence for dibenzyl (GLC and NMR). The *N*-(1-phenylethyl)amide (**15**) gave a mixture of acid and ester similar to the benzene solution results.

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References and Notes

(1) For paper 14, see R. S. Givens and B. Matuszewski, *J. Am. Chem. Soc.*, **97**, 5617 (1975). A preliminary account of this work was presented at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6–11, 1975, Abstract ORGN 100.

(2) (a) On leave from A. Mickiewicz University, Poznan, Poland (1974); (b) Undergraduate research participant.

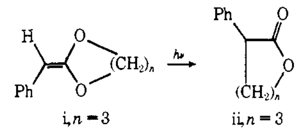
(3) For leading references see: (a) M. L. Kaplan and E. A. Truesdale, *Tetrahedron Lett.*, 3665 (1976); (b) D. A. Jaeger, *J. Am. Chem. Soc.*, **97**, 902 (1975); **96**, , 6216 (1974); (c) V. B. Ivanov, V. L. Ivanov, and M. G. Kuzmin, *Mol. Photochem.*, **6**, 125 (1974); (d) T. O. Meiggs, L. I. Grossweiner, and S. I. Miller, *J. Am. Chem. Soc.*, **94**, 7981, 7986 (1972); (e) F. R. Stermitz and W. H. Huang, *ibid.*, **93**, 3427 (1971); (f) H. Javaheripour, M. Sun, and D. C. Neckers, unpublished results; (g) S. Fujita, Y. Ozaki, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **45**, 2571 (1972); (h) J. Libman, M. Sprecher, and Y. Mazur, *J. Am. Chem. Soc.*, **91**, 2062 (1969); (i) A. E. Greene, J.-C. Muller, and G. Ourisson, *Tetrahedron Lett.*, 4147 (1971); G. W. Perold and G. Ourisson, *ibid.*, 3871 (1969).

(4) R. S. Givens and W. F. Oettle, *J. Org. Chem.*, **37**, 4325 (1972); *J. Am. Chem. Soc.*, **93**, 3301 (1971).

(5) R. S. Givens, B. Matuszewski, and C. V. Neywick, *J. Am. Chem. Soc.*, **96**, 5547 (1974).

(6) (a) P. S. Engel, *J. Am. Chem. Soc.*, **92**, 6074 (1970); (b) R. H. Eastman and W. Robbins, *ibid.*, **92**, 6076 (1970).

(7) R. S. Givens and B. Matuszewski, unpublished results.
(8) (a) This probe was chosen over other conventional approaches for several reasons, e.g., (1) changing to more viscous solvents, solvents with extractable hydrogens would be necessary, complicating the reaction product mixture; and (2) trapping agents such as oxygen that would react with the radicals also quench the excited singlet state of **3**.[5] (b) The ***h*** notation indicates unlabeled ester; ***d***, deuterium-labeled ester; ***O***, oxygen-18 labeled ester.
(9) K. Biemann, "Mass Spectrometry", McGraw-Hill, New York, N.Y., 1962, p 224ff. The ^{18}O or D content was determined by directly inserting the labeled sample into the inlet of the Varian-MAT CH5 mass spectrometer. The ionization energy was 70 eV unless otherwise indicated and the inlet temperature, approximated 220 °C. The ^{18}O content was determined from the P/(P + 2) peak heights as measured on the photographic output.
(10) P. Sabatier and M. Murat, *Ann. Chim. (Paris)*, **4**, 253 (1915).
(11) The extensive studies of White (W. J. le Noble, E. H. White, and P. M. Dzadzic, *J. Am. Chem. Soc.*, **98**, 4020 (1976) and references cited therein) have shown that separated carboxylate–carbonium ion pairs can be generated from *N*-nitrosoamides.
(12) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).
(13) A number of other photodecarboxylations have been reported (for esters, anhydrides, and acids) where radical intermediates are suggested. (See ref 3a,e,f,g, and also A. Zweig, *Pure Appl. Chem.*, **33**, 389 (1973), and references cited therein.)
(14) The decay process may be by way of the triplet manifold. No attempt was made to measure intersystem crossing efficiencies.
(15) (a) H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963); (b) H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963). (c) The higher value reflects the material balance for the starting ester disappearance. Although no other products were formed, only 80% of the product was isolated in preparative runs.
(16) This indirectly lends support for a $_{\pi}2_s + {}_{\sigma}2_s$ migration of the benzyl carbon. An interesting parallel is found in the work of J. E. Baldwin and L. E. Walker (*J. Am. Chem. Soc.*, **88**, 3769 (1966)), where the more flexible i photorearranged to a α-phenyl-γ-valerolactone (ii), while iii failed to give any α-phenyl-γ-butyrolactone (iv).



i, $n = 3$
iii, $n = 2$

ii, $n = 3$
iv, $n = 2$

(17) M. Schneider and H. Strohacker, *Tetrahedron*, **32**, 619 (1976).
(18) (a) E. H. White, R. H. McGirk, C. A. Aufdermarsh, Jr., H. P. Tiwari, and M. J. Todd, *J. Am. Chem. Soc.*, **95**, 8107 (1973); (b) E. H. White and C. A. Elliger, *ibid.*, **89**, 165 (1967); (c) E. H. White, *ibid.*, **77**, 6014 (1955).
(19) C. S. Marvel, "Organic Syntheses", Collect. Vol. 3, Wiley, New York, N.Y., 1955, p 495.
(20) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).
(21) Southern New England Co., Middletown, Connecticut.
(22) The procedure used was patterned after the work of Kice et al. (*J. Am. Chem. Soc.*, **92**, 5608 (1970)).
(23) The alcohol ($[\alpha]^{35}{}_{D}$ $-42°$) was resolved as the brucine salt of the phthalate half ester according to the method of Kenyon (E. Downer and J. Kenyon, *J. Chem. Soc.*, 1156 (1939)).
(24) The *N*-(1-phenylethyl)phenylacetamide was synthesized from 1-phenylethylamine (Aldrich Chemical Co., $[\alpha]^{20}{}_{D}$ +39 (neat)). Specific rotations for the amide were +105.8 (589 nm), +106.3 (573.8), +123.8 (546), +230.4 (436), and +406.0 (365).
(25) The specific rotations were not measured because of the instability of **15**.

Metathesis of Cyclic and Acyclic Olefins[†]

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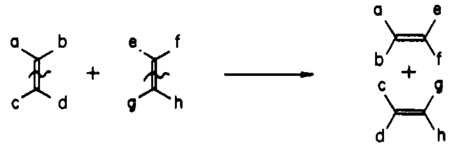
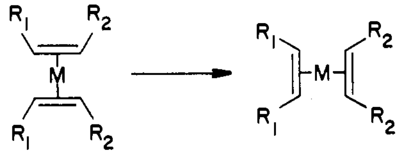
Abstract: Two experimental tests were made to determine whether the mechanism of the olefin metathesis reaction is that indicated in eq 7 or that indicated in eq 3. In one set of experiments, cyclooctene, 2-butene, 4-octene, and a molybdenum-containing catalyst were combined. The distribution of products in equation 4 was analyzed as close to the start of reaction as possible and extrapolated to measure the product ratios at zero time. Calling the ratio at zero time $[C_{14}]/[C_{12}] = r_1$ and $[C_{14}]/[C_{16}] = r_2$, the product $\overline{r_1 \times r_2}$ was measured as 4.05 ± 0.05 which is in accord with the mechanism in eq 3 and contrary to that in eq 7 no matter whether the first or the second step is rate-determining. The kinetics are analyzed to show how the relative reactivities of two acyclic olefins reacting according to eq 3 can be measured. In the experiments above the ratios of the rate constants for *trans*-2-butene and *trans*-4-octene are 3.08 ± 0.16, for *cis*-2-butene and *cis*-4-octene 6.46 ± 0.87. In another set of experiments, cyclooctene, 2-hexene, and a molybdenum-containing catalyst were combined, and the distribution of the products in eq 5 were analyzed at zero time. It is shown that the ratios of the "triads" of products, like C_{12}, C_{14}, and C_{16}, should be $1{:}r{:}1$, where $r = (k_3/k_4) + (k_4/k_3)$ and k_3 and k_4 are the rate constants for the two possible reactions, according to eq 14, of an olefin with a metal carbene. For the experiment performed here with 2-hexene, r is 3.25, but it is shown that for less symmetrically substituted olefins r should be, and is, much larger. A procedure is developed for measuring the relative reactivities of cyclic and acyclic olefins.

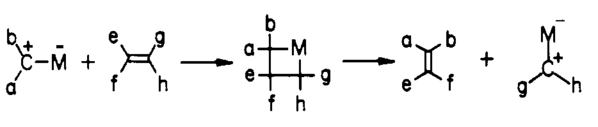
That the mechanism of the olefin metathesis reaction (eq 1), initially thought on the basis of the gross structural change to involve the union of two olefin molecules (eq 2),[1] is instead a chain reaction propagated by the union of an olefin with a metal carbene (eq 3),[2] was first indicated by the distribution of products when both cyclic and acyclic olefins react or form in metathesis. Other evidence has since supported this view.[3]



(1)



(2)



(3)

In this paper we consider two of the original experimental tests of the mechanism, the distribution of products in the reactions summarized in eq 4 and 5. The background of the experiments and a summary of the results were reported previously;[2a] the details both of the measurements and of the IR analysis are reported here.

[†] Dedicated to Professor R. B. Woodward on his sixtieth birthday.