ane is 1.114 ± 0.003.[2] The similarities of these α-D effects suggest similar transition states, i.e., for I intramolecular rate limiting capture of II by the internal carboxylate ion ($k_{-1} > k_2$, $k_c > k_2$, k_c rate-limiting).

While an example of an SN2 displacement at benzal carbon has not yet been reported related studies[4] suggest that such a "tight" transition state should exhibit an α-D effect which is *smaller* than that observed[2] for rate-limiting attack on an ion-pair intermediate. Thus, the magnitude of the α-D effect for I in 40–70% dioxane is inconsistent with attack of internal carboxylate ion on covalent chloride[5] (k_{intra}, Scheme I).

Unlike the results obtained in pure water the α-D effect for the lithium salt of I in 50% dioxane is slightly larger, 1.149 ± 0.005. We expect that extensive ion pairing exists between the metal ion and the carboxylate ion in this solvent and some dependence of the α-D effect on the nature of the metal ion is expected for a rate limiting k_c process. However, addition of 0.20 *M* $LiClO_4$ in this solvent results in a rate *reduction* ($k_{\text{salt}}/k_0 = 0.82$) and an *unchanged* α-D effect, 1.148 ± 0.005. This inverse salt effect and a very small m[6] ($m = 0.13$, Figure 1) in the less polar solvent mixtures suggest a much less polar transition state for I in >40% dioxane compared with water. The fact that the α-D effect is unchanged upon addition of $LiClO_4$ is consistent with rate-limiting intramolecular capture of the carbonium ion occurring at the intimate ion-pair stage. Had nucleophilic capture occurred at the solvent-separated ion-pair stage (III) addition of $LiClO_4$ would have prevented return from this intermediate thereby increasing the α-D effect.[2]

With a view toward understanding the role of ASP-52 in the mechanism of action of lysozyme[7] we have recently studied[8] the hydrolysis of I and its para isomer. In this study no rate enhancement was observed for the *o*-carboxy substituent in water although k_{ortho} exceeded k_{para} by 50-fold in 50% aqueous dioxane. This increased rate of hydrolysis of I over its para isomer in the less polar solvents is now seen to result from the incursion of a new mechanism available to I which is not possible for its para isomer. The question of electrostatic stabilization of a resonance stabilized carbonium ion intermediate by a proximate carboxylate ion remains.[7] A comparison of k_1 for I and its para isomer would, of course, resolve this question but such a comparison is not yet possible in this system.

Acknowledgment. We thank Professors D. L. Whalen and R. M. Pollack for penetrating discussions throughout the course of this work. Financial support from the National Science Foundation (GP-37701) and the National Institutes of Health (GM-21933) is gratefully acknowledged.

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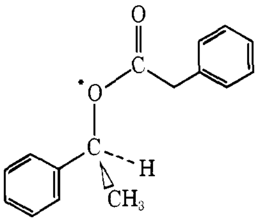
Photodecarboxylation. A Labeling Study. Mechanistic Studies in Photochemistry. XIV[1]

Sir:

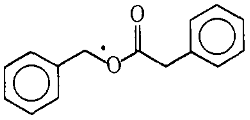
We wish to report a *novel, stereospecific oxygen scrambling reaction which occurs in competition with the photodecarboxylation reaction of aryl methyl esters.* Parallel studies with oxygen-18 labeled esters and with (*S*)-(−)-α-methylbenzyl phenylacetate (**1**) demonstrate the occurrence of this "hidden", stereospecific process.

Previously, we[2] and others[3] have shown that aryl methyl esters photodecarboxylate with efficiencies ranging from 0.3 to less than 5.7×10^{-3}. Product analyses[2] and mechanistic studies[2,3a] indicate that radical intermediates are generated by irradiation of arylmethyl phenylacetates (e.g., **2–4**). In a few cases, cage effects are clearly implied.[2]

In contrast, reports[4] on the photochemistry of di-*m*-methoxybenzyl acetate and analogous esters suggest ionic intermediates are generated. A recent study has noted that recombination of the initially formed intermediates occurs by a nonstereospecific pathway.[5]



(S)-(−)-1



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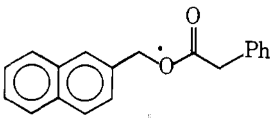

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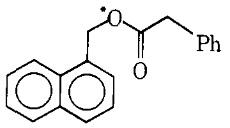

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Our results show that, for the arylmethyl phenylacetates, this recombination reaction is a major pathway and is completely stereospecific. Thus, ^{18}O-labeled alcohols (from reduction of the acid catalyzed $H_2{}^{18}O$ exchange of the corresponding carbonyl compound) were esterified with phenylacetyl chloride in pyridine. The ^{18}O labeled esters (**1–4**) were irradiated to partial conversion; the unreacted ester was isolated and reduced with LAH, and the product alcohols were separated and analyzed by mass spectrometry. As evidenced by the results listed in Table I, scrambling of the label from the ether oxygen to the carbonyl oxygen occurs for α-methylbenzyl phenylacetate (**1**) and benzyl phenylacetate (**2**), and for the two naphthyl esters **3** and **4**. Without the label, this reaction would go undetected.[6]

Because our earlier mechanistic analysis for esters **2–4** was predicated on the assumption that recombination of the initially formed radical pair did not occur,[6] the efficiency of the scrambling reaction was of interest. The low efficiency for naphthylmethyl esters **3** and **4** ($\Phi_\beta = 0.055$ and $\Phi_\alpha =$

Table I. Oxygen-18 Distribution before and after Irradiation of Esters 1–4

Ester	hr	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	Scrambling quantum yield[d]	Total quantum yield
1	—	0	0.238 ± 0.028	5.868 ± 0.206	—	—		
	2.5	50	*e*	4.880 ± 0.189	35	*e*	*f*	*f*
2	—	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 ± 0.28	3.485 ± 0.248	—	—	(0.16)[g]	0.22
	6	12	0.596 ± 0.44	2.881 ± 0.162	37	24	0.14	
	10	25	0.863 ± 0.52	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	
4	—	0	0.195 ± 0.020	2.005 ± 0.142	—	—	(0.04)[g]	0.05
	6	1.8	0.289 ± 0.020	1.937 ± 0.117	7	9	0.03	
	10	3	0.358 ± 0.029	1.685 ± 0.089	35	17	0.05	
	17	5	0.426 ± 0.014	1.657 ± 0.193	38	25	0.04	

[a] Benzyl esters were irradiated in dioxane at 253.7 nm; naphthylmethyl esters in benzene at 300 nm. Solutions of ca. $10^{-2}M$ were degassed with N_2 and irradiated in a merry-go-round apparatus (Southern New England-RPR-100) 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 LAH reduction of the esters. [c] Calculated from the change in the ^{18}O per cent of the alcohols after irradiation. [d] As determined from eq 1 using ϕ's from ref 2a and 2d. [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.

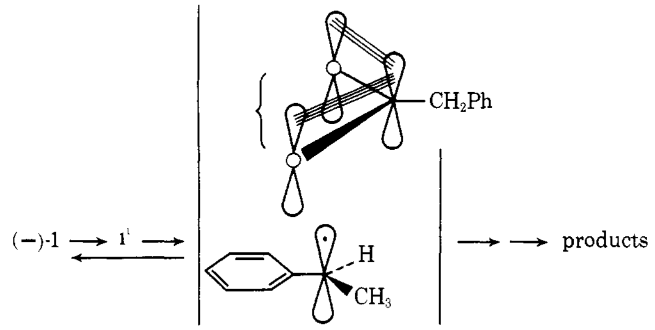
0.005) can be partially attributed to an intervening, more efficient scrambling reaction. That this was a major pathway for these esters is evident from the quantum yields calculated from the following expression and given in Table I.

$$(\%\ \text{scrambling})/(\%\ \text{conversion}) = \Phi_c/\Phi_{dis} \qquad (1)$$

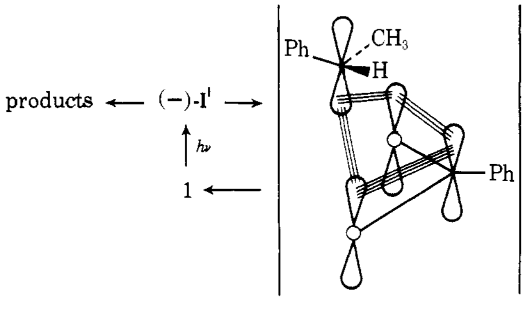
where Φ_c and Φ_{dis} are the quantum yields for scrambling and disappearance, respectively. Further analysis reveals that the order of the relative reactivities of the two naphthyl methyl esters remains, now by a factor of ca. 4, and accords with our earlier observation of a reversal of ground state reactivity.[2a]

Because the previous studies on ^{18}O equilibration were performed on achiral esters, this study was expanded to include α-methylbenzyl phenylacetate (**1**), which would allow observation of both stereochemical and ^{18}O scrambling. As shown in Table I, facile ^{18}O scrambling does occur. The stereochemical integrity, however, was essentially intact as noted from the rotation of the ester before ($[\alpha]^{35°}{}_{436}$ $-121.8 \pm 0.8°$) and after irradiation ($[\alpha]^{35°}{}_{436}$ $-118.0 \pm 2.9°$).[7,8]

Among the several possible mechanistic schemes for the scrambling of the oxygen functions, two are particularly attractive. In accord with the cage effects seen for product formation,[9] a parallel cage effect on recombination of initially generated radical pairs is possible. However, the cage effect has the additional requirement of maintaining the asymmetry of the species generated, e.g.,



A second, equally attractive pathway involves a 1,3 sigmatropic migration of the benzyl moiety as a competing pathway for the excited singlet e.g.,



By either pathway, however, the return to starting ester has proven to be a competing reaction accounting for a significant fraction of the inefficiency of the decarboxylation process.

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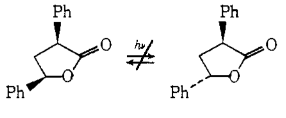

(7) Determined by two runs (50 and 56% conversion) with three determinations per run.

(8) This contrasts with the results reported by Jaeger (see footnote 19, ref 5) in which racemization is reported for the (−)-3,5-dimethoxybenzyl-*l*-*d* acetate photolysis, yet recombination is clearly occurring.

(9) A study of the products from photodecarboxylation of mixtures of dideuterated **3** and nondeuterated **3** revealed a mixture of mono-, di-, and trideuterated 1-β-naphthyl-2-phenylethanes in a ratio of 1:11:1. This can

be dissected into 30% noncage and 70% cage reaction of the arylmethyl radicals (unpublished results of B. Matuszewski and D. Leung).
(10) On leave from A. Mickiewicz University, Poznan, Poland.

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Cation and Electrolyte Concentration Effects on Equilibria and Kinetics of Processes Involving Disproportionation of Radical Ions

Sir:

Our recent measurements of reversible electrode potentials[1] for both the first and second charge transfers to aromatic hydrocarbons in tetrahydrofuran (THF) in the presence of various tetraalkylammonium salts gave results in sharp contrast to those reported by Rainis and Szwarc for potentiometric titrations using sodium biphenylide.[2] Our inability to make reversible potential measurements in the presence of sodium ion at that time made it impossible to determine whether the discrepancies were due to experimental error or if a large cation effect on disproportionation equilibria was operative. The experimental difficulties have since been resolved and we now report substantial differences between potentials measured in the presence of sodium ions and tetraalkylammonium ions as well as a significant effect of cation concentration. The latter is especially important since it may be used as a powerful tool in evaluating possible disproportionation mechanisms of radical ions.

The measurement of reversible potentials for the reduction of most aromatic hydrocarbon radical anions in the presence of sodium ion at a mercury electrode is precluded by the reversible reduction of sodium ion at a potential less negative than necessary to reduce the radical ions. Difficulties were also encountered[1] during attempts to use micro platinum electrodes for the measurements. We have now found that both platinum and glassy carbon electrodes are suitable for the measurements when freshly polished and when oxygen is completely removed from the electrolytic solutions. In order to obtain reversible potentials the measurements were conducted in solutions which were in contact with active alumina, a procedure which removed trace impurities that react with the highly reactive dianions.[1,3] The voltammetric measurements were made in the manner previously described.[1,4]

Data for the reversible reductions of perylene (PE) and anthracene (AN) in THF, 1,2-dimethoxyethane (DME), and dimethylformamide (DMF) are summarized in Table I. The disproportionation equilibrium constants (K_{disp}) at 11°C are calculated according to eq 1.

$$0.057 \log K_{\text{disp}} = E_2 - E_1 = \Delta E^0 \qquad (1)$$

The reversibility of the two consecutive charge transfers to PE in the presence of sodium ions is demonstrated by the cyclic voltammogram in THF (Figure 1) where E_1 and E_2 refer to the peak potentials for the first and second charge transfers, respectively. The difference in peak potential, $E_2 - E_1$, for reversible charge transfers may be equated to the difference in formal potentials, ΔE^0. The effect of Na^+ concentration on ΔE^0 for the two reduction stages of PE in THF is demonstrated by the data in Figure 2. Over the concentration range of $NaBPh_4$ investigated ΔE^0 increased linearly with the logarithmic increase in the salt concentration according to eq 2.

$$(\Delta E^0) = (\log C_{Na^+})66 \text{ mV} \qquad (2)$$

Table I. Solvent, Cation, and Cation Concentration Effects on Disproportionation Equilibria

Compound	Solvent	Cation	[Cation], M	ΔE^0, mV[a]	K_{disp}
Perylene	THF	Na^+	0.07	380	1.7×10^{-7}
		Bu_4N^+	0.22	550	1.6×10^{-10}
	DME	Na^+	0.04	540	4.1×10^{-10}
		Bu_4N^+	0.20	555	7.6×10^{-10}
	DMF	Na^+	0.20	605	5.9×10^{-11}
		Bu_4N^+	0.20	595	3.9×10^{-11}
Anthracene	THF	Na^+	0.07	300	2.2×10^{-6}
		Bu_4N^+	0.22	685	1.6×10^{-13}
	DME	Na^+	0.04	470	2.3×10^{-9}
		Bu_4N^+	0.50	700	2.9×10^{-13}
	DMF	Na^+	Not reversible		
		Bu_4N^+	0.20	750	2.2×10^{-14}

[a] Difference in reversible peak potentials for first and second charge transfer, temperature 11°C.

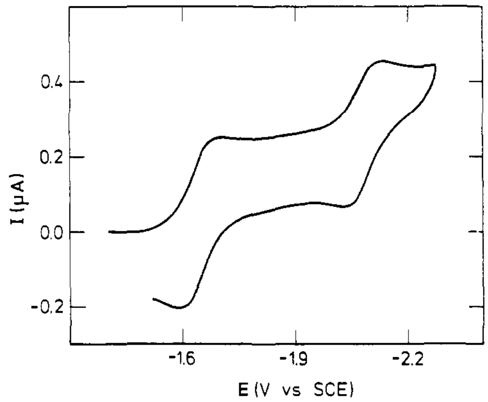

Figure 1. Cyclic voltammogram for the reduction of perylene in THF ($NaBPh_4$ = 0.07 M). Voltage sweep rate = 150 mV/sec. Temperature = 11°.

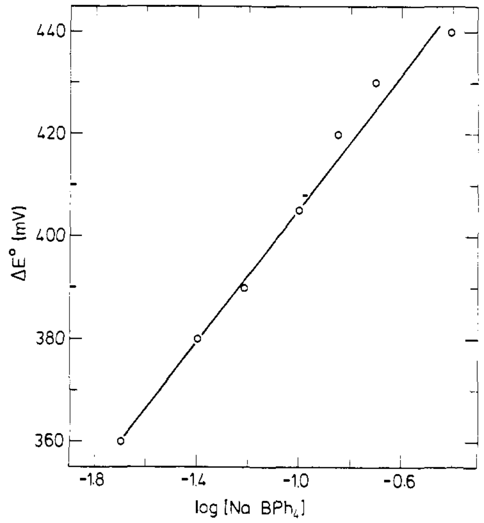

Figure 2. The effect of [$NaBPh_4$] on ΔE^0 for the reduction of perylene in THF.

The data are extrapolated to a constant sodium ion concentration (0.02 M) in Table II and compared to that available from potentiometric titrations.[2] The slope of the ΔE^0 vs. log [Bu_4NBF_4] for the reduction of PE in DME was also found to be equal to 66 mV. The difference in formal potentials