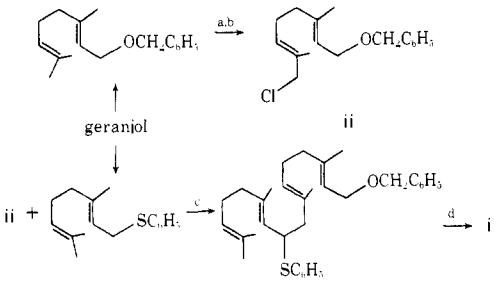
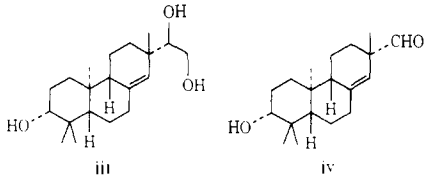
er, *Tetrahedron*, **28**, 3155 (1972), and references included therein.
(3) A. J. Birch, R. W. Rickards, and H. Smith, *Proc. Chem. Soc., London*, 192 (1958).
(4) 14,15-Oxidogeranylgeraniol was prepared by terminal oxidation of geranylgeraniol(ii),[1c] in turn made readily available by a synthesis developed in this laboratory:



where (a) SeO_2–95% EtOH; (b) MeLi, TsCl, LiCl; (c) C_4H_9Li–THF; (d) Li/Na–$EtNH_2$.
(5) (a) P. A. Stadler, A. Eschenmoser, H. Schinz, and G. Stork, *Helv. Chim. Acta*, **40**, 2191 (1957); (b) R. Lees, Ph.D. Dissertation, Stanford University, 1972, and references therein.
(6) Comparison compound was prepared by sodium periodate cleavage of darutigenol (iii) to aldehyde (iv),[7] followed by conversion with methylene triphenylphosphine to 13-epi **7c**, which was transformed by treatment with HCl–$CHCl_3$ to 13-epi **7b**.[8]



(7) A. Diara, C. Asslineau, and E. Lederer, *Bull. Soc. Chim. Fr.*, **27**, 2171 (1960).
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(10) C. R. Enzell and B. R. Thomas, *Acta Chem. Scand.*, **19**, 1875 (1965), and references included therein.
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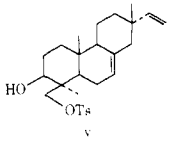

(12) Cf. K. B. Sharpless, R. F. Lauer, O. Repic, A. Y. Teranishi, and D. R. Williams, *J. Am. Chem. Soc.*, **93**, 3303 (1971).

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Deuterium Isotope Effects in the Solvolysis of Benzal Chlorides. II. Evidence for a Change in Mechanism in the Hydrolysis of *o*-Carboxybenzal Chloride in Water and Water–Dioxane Mixtures

Sir:

The relevance of the mechanisms of neighboring group participation to problems of enzymatic catalysis has been documented and continues to be a topic of interest to physical organic chemists.[1]

In this communication we wish to report that *o*-carboxybenzal chloride (I) hydrolyzes in water and in dioxane–water mixtures containing greater than 40% (by volume) dioxane by two distinct mechanisms.

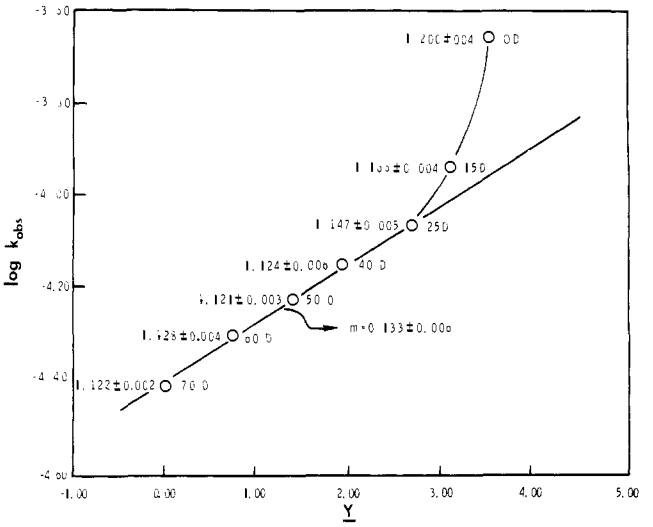
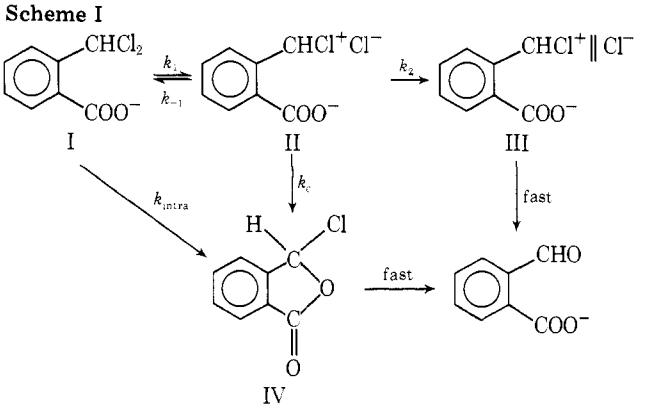


Figure 1. First-order rate constants for the hydrolysis of *o*-carboxybenzal chloride determined spectrophotometrically by monitoring the appearance of aldehyde at 257 mμ at 25° as a function of solvent polarity, Y. [NAOH] = 0.10 *M* for all solvents except water. For water [NAOH] = 0.20 *M*. Numbers to the left of each datum point refer to the α-D isotope effect determined under these conditions. Numbers to the right of each datum point refer to the volume per cent dioxane in the solvent, e.g., 70 D = 70% dioxane–30% water = 70 ml of dioxane + 30 ml of water.

In water the hydrolysis of I involves rate determining interconversion of ion-pair intermediates (k_2, Scheme I)

Scheme I



whereas in 40–70% aqueous dioxane the rate-determining step is intramolecular capture of the intimate ion-pair (II) by the neighboring carboxylate ion (k_c, Scheme I).

The α-D isotope effect observed for the sodium salt of I in water (1.200 ± 0.004, Figure 1) is the *maximum* value for benzal chlorides[2] and we, like Shiner,[3] interpret this result in terms of a transition state involving no covalent attachment of leaving group or incoming nucleophile (k_2, Scheme I). As expected for this mechanism the α-D effect for the lithium salt of I in water is unchanged, 1.197 ± 0.006. Addition of 0.20 *M* $LiClO_4$ in this solvent results in a modest rate increase (the expected normal salt effect, k_{salt}/k_0 = 1.09) and an unchanged α-D effect, 1.198 ± 0.009. Thus, in water, $k_{-1} > k_2$, $k_2 > k_c$, and k_2 is rate-limiting.

In the less polar dioxane–water mixtures the situation is quite different. In the range 40–70% dioxane the α-D effect for the sodium salt of I is much smaller, 1.124 ± 0.005. This α-D effect is consistent with a transition state involving substantial covalent bonding at the isotopically labeled position. For example, the α-D effect for rate limiting attack of solvent on the solvent-separated ion pair in the hydrolysis of *p*-methoxybenzal chloride in 85% aqueous diox-

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* ($k_{salt}/k_0 = 0.82$) 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.

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(4) Reference 3, p 137.
(5) The α-D effects observed for the lithium and sodium salts of I in solvents containing greater than 40% (v/v) dioxane are also consistent with k_1 rate limiting ($k_c > k_{-1}$, $k_c > k_2$). However, extrapolation of the data in the less polar dioxane–water mixtures (40–70% dioxane) to pure water affords an extrapolated rate for water which is *less* than the observed rate. Since k_{obsd} cannot exceed k_1 in any solvent [k_{obsd} = (fraction of intermediate which leads to product)k_1] k_1 cannot be rate limiting in 40–70% aqeous dioxane. For a related example in the solvolysis of a neopentyl derivative see V. J. Shiner, Jr., and W. Dowd, *J. Am. Chem. Soc.*, **91**, 6528, 7748 (1969); W. M. Schubert and P. H. LeFevre, *ibid.*, **94**, 1639 (1972).
(6) This should be compared to $m = 1.3$ for the hydrolysis of benzal chloride in dioxane–water mixtures; B. Colina, M. G. Rotaeche, E. Guerrero, A. M. Alpica, M. Calzadilla, and J. Baumrucker, *J. Org. Chem.*, **39**, 3918 (1974).
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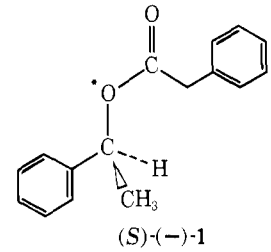
Photodecarboxylation. A Labeling Study. Mechanistic Studies in Photochemistry. XIV[1]

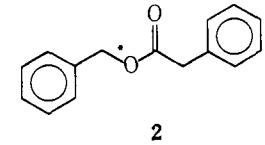
Sir:

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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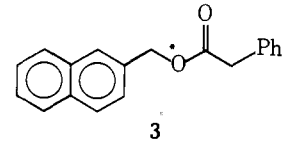
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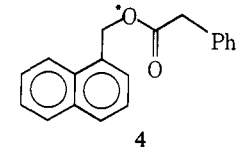
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Our results show that, for the arylmethyl phenylacetates, this recombination reaction is a major pathway and is completely stereospecific. Thus, ^{18}O-labeled alcohols (from reduction of the acid catalyzed $H_2{}^{18}O$ exchange of the corresponding 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 $\Phi_\alpha =$