alternative predominated, as would be expected for an ionic reaction. Careful elution chromatography of the products led to the isolation of IIc (Y = OMe; 20%), mp 111° (lit.[11] 111–112°), identical with the ether obtained by successive treatments of 1,1,3-triphenylpropanol[12] with potassium metal in toluene and methyl iodide. Other products included 1,1,3-triphenylpropene (10%) and benzhydryl methyl ether (7%), but no ether IX could be detected by the methods used.

Interestingly, conversion to ether IIc (Y = OMe) was doubled when Ic was irradiated in methanol–acetic acid (equimolar), and neither IX nor the expected acetate IIc (Y = OAc) was isolated. However, a low conversion (10–12%) to IIc (Y = OAc), mp 128–130°, was observed when pure acetic acid was used as the solvent. The structure of IIc (Y = OAc) rests on its infrared [$\nu_{max}^{CS_2}$ 1745 (vs), 1240 (vs), 1215 cm^{-1} (vs)] and nmr [τ^{CDCl_3} 2.5–3.0 (15 protons), 6.6–7.05 (two-proton multiplet), and 7.35–7.8 (two-proton multiplet)] spectra as well as elemental analysis.

We believe that the increase in conversion to IIc (Y = OMe) when acetic acid was present was probably a solvent effect rather than acid catalysis, since this phenomenon was not observed with the diphenylcyclopropane Ia. Irradiation of Ia in methanol–acetic acid resulted in a reduced conversion to IIa (Y = OMe) (30%) and gave 8% of the acetate IIa (Y = OAc). Base catalysis does not seem to occur either, as the conversion of Ic to IIc (Y = OMe) in methanol–benzene containing 0.1 *M* sodium methoxide was the same as in the absence of the base.

Preliminary attempts to quench or sensitize the photocleavage reaction have failed. Neither oxygen (vessel open to air)[13] nor naphthalene (0.001 *M*) had any detectable effect on the formation of IIa (Y = OMe). No ether IIa (Y = OMe) was obtained when a solution of Ia (0.1 *M*) and acetophenone (1.9 *M*) in methanol was irradiated with 3500-A light.

Benzene (43%) was without effect on the formation of the triphenyl ether IIc (Y = OMe), but reduced the conversion of the diphenylcyclopropane Ia to IIa (Y = OMe) in 24 hr from 40 to about 15%, perhaps simply by screening Ia from most of the light.

1,1,2,2-Tetraphenylcyclopropane in methanol photolyzed essentially completely to diphenylcarbene (trapped as benzhydryl methyl ether) and 1,1-diphenylethylene, as reported elsewhere,[4] and no 1,1,3,3-tetraphenylpropyl methyl ether could be isolated.

1,1-Diphenylcyclopropane did not undergo the heterolytic cleavage reaction under these conditions. Irradiation of this cyclopropane in deuteriomethanol gave 1,1-diphenylpropane and 1-phenylindan (IV).

The reaction is apparently rather sensitive to the nature of the substituents on the three-membered ring. The fact that O–H bonds rather than the weaker C–H bonds are broken, the solvent effects, and the direction of addition to Ic all point convincingly to the reaction being ionic rather than radical in nature.

There seems to be no clear precedent for this reaction with the possible exception of the photoreaction of [2.2]paracyclophane with alcohols to give ethers reported by Helgeson and Cram[14] while this work was in progress. The photoaddition of alcohols to certain olefins[15] may be a related phenomenon.

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Asymmetric Oxidation of Thioethers to Sulfoxides. Configurational Specificity Induced by Optically Active Organic Catalysts[1]

Sir:

There have been several recent efforts made to oxidize unsymmetrical thioethers stereospecifically to optically active sulfoxides. For example, this has been achieved through microbial oxidation[2] and by employing optically active peracids as the oxidant.[3] We wish to report asymmetric formation of sulfoxides through mediation of simple optically active catalytic species.

The oxidation of alkyl sulfides (**1**; R = R′ = alkyl) to alkyl sulfoxides (**4**; R = R′ = alkyl) by iodine has been reported as being catalyzed by nucleophiles such as phosphate and phthalate ions.[4] It has been proposed that the catalyst (*e.g.*, phthalate ion) reacts with an iodosulfonium ion (**2**; R = R′ = alkyl) to give an acylsulfonium complex (**3**; R = R′ = alkyl) which then decomposes to give an alkyl sulfoxide (**4**; R = R′ = alkyl) plus an acid derivative (*e.g.*, phthalic anhydride).

We have found, for example, that at 25° the oxidation by iodine (0.00077 mole, and 0.00154 mole of potassium iodide) of benzyl methyl sulfide (0.00077 mole) suspended in 90 ml of *d*-2-methyl-2-phenylsuc-

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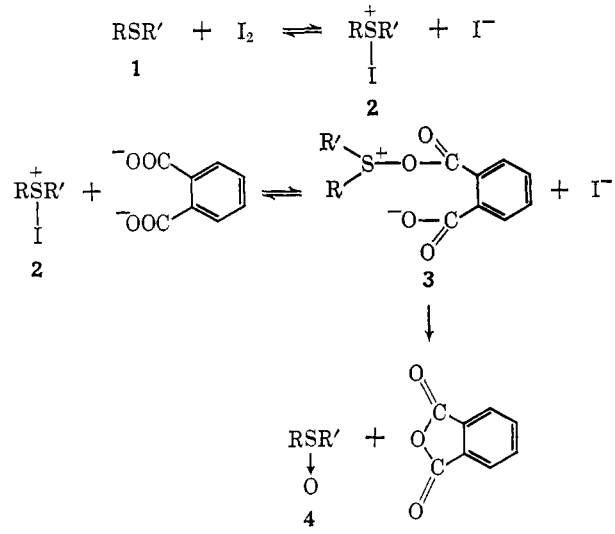

cinate[5] buffer (0.064 *M*), at pH 6.0, yielded optically active benzyl methyl sulfoxide (**4**; R = Me, R′ = PhCH$_2$), [α]D +3.5° in chloroform and −6.1° in 95% ethanol. The optical purity of the product, with respect to the isomer with the (*R*) configuration, was 6.36% from measurements in chloroform and 6.35% from measurements in 95% ethanol. These percentages were based on the reported[6] specific rotation of the pure isomer with the (*S*) configuration ([α]D −55° in chloroform and +96° in ethanol).

Although the above oxidation reaction was more than 97% complete after 7 hr, a similar optical yield of the isomer with the (*R*) configuration was obtained whether the reaction mixture was left for 6 hr or for 60 hr before the sulfoxide was extracted. Thus, racemization of the optical isomers of the sulfoxide did not occur to an appreciable extent under the experimental conditions.

When phthalate buffer (0.064 *M*) was used as the oxidation catalyst instead of the *d*-2-methyl-2-phenylsuccinate buffer, the reaction yielded optically inactive benzyl methyl sulfoxide.

From a consideration of other dissymmetric tricoordinate sulfur compounds,[7] the iodosulfonium ion **2** (R = Me, R′ = PhCH$_2$) is expected to be a racemic mixture of two optically active enantiomeric forms. These would be expected to react at different rates with the optically active reagent, *d*-2-methyl-2-phenylsuccinate ion.

While the absolute configuration of *d*-2-methyl-2-phenylsuccinic acid has not been proved, comparison of ORD curves suggests it has the same configuration as (+)-(*S*)-phenylsuccinic acid.[8]

Because the yield of benzyl methyl sulfoxide (**4**; R = Me, R′ = PhCH$_2$) from the over-all reaction is greater than 97%, and the product was only 6.4% richer in one optical isomer than the other, either the rates of the attack of the nucleophilic asymmetric catalyst on the two enantiomorphic forms of the iodosulfonium species are quite similar, or the indicated equilibrium leading to formation of the acylsulfonium species coupled with the relative rates of cyclic anhydride formation from the two optically active intermediates provide only a limited degree of specificity. Iodide dependence of the over-all reaction kinetics appears to favor the first alternative. However, this optically specific synthesis provides strong evidence that the role of the catalyst in the postulated reaction scheme is correct. An analogy between the above synthesis and a stereospecific enzymic reaction appears particularly apt, especially since, in the former, the energy of oxidation appears to be transfered to the catalyst.[4] Details of these experiments, including ultraviolet spectra, ORD curves, and description of other sulfide systems, will be presented separately.

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(5) The sample of *d*-2-methyl-2-phenylsuccinic acid ([α]D +22.6° in 95% ethanol) used in this study was kindly donated by Parke, Davis and Co. of Detroit, Mich. This sample is estimated to have an optical purity of 80% based on the specific rotation of pure *d*-2-methyl-2-phenylsuccinic acid ([α]D +28.3° in 95% ethanol, mp 150.5°) and pure *l*-2-methyl-2-phenylsuccinic acid ([α]D −28.5° in 95% ethanol, mp 150.5°). An equimolar mixture of the pure enantiomers melts at 163° compared to the true racemate, mp 157–158° (P. A. S. Smith, *J. Am. Chem. Soc.*, 71, 3418 (1949)), 163–164° (H. Le Moal, A. Foucaud, R. Carrié, J. Hamelin, and C. Sévellec, *Bull. Soc. Chim. France*, 579 (1964)), and 167° (G. Poulain, *ibid.*, 913 (1964)).

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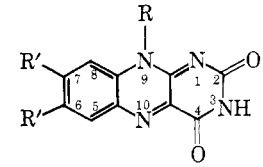
The Participation of the Hydroxyl Group in the Photobleaching of 9-(2′-Hydroxy-2′-methylpropyl)isoalloxazine[1]

Sir:

As part of a photochemical study on model flavin compounds, we have studied the photobleaching of 9-(2′-hydroxy-2′-methylpropyl)isoalloxazine (Ic). Experimental results are presented which demonstrate the participation of the hydroxyl group in this photoreaction.

Halwer[2] studied the photobleaching of 9-(2′-hydroxyethyl)isoalloxazine (Ib) and Ic and concluded on the basis of general acid catalysis that the 2′-hydroxyl group was active in the photoreaction. However, since Halwer's work was published it has been well established that alcohols donate hydrogens from the α carbon during intermolecular photoreduction reactions if they are available.[3,4] Kinetic isotope effects[5] of 2.8 and 2.7 were found for the photoreduction of benzophenone with 2-propanol-2-*d* and benzhydrol-α-*d*, respectively. Photochemical studies on riboflavin (Ia) and Ib have again confirmed this concept.[6,7] A



Ia, R′ = CH$_3$; R = ribityl
b, R′ = H; R = CH$_2$CH$_2$OH
c, R′ = H; R = CH$_2$C(CH$_3$)$_2$OH

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