Acknowledgment. We are indebted to Dr. E. Gil-Av for stimulating discussions concerning vapor phase chromatography.

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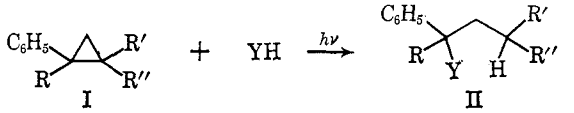
Heterolytic Photocleavage of Cyclopropanes

Sir:

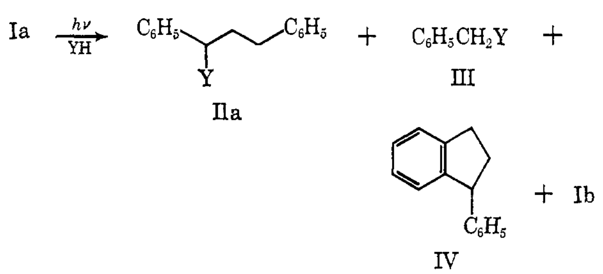
Previous communications from our laboratories have described a number of photochemical reactions of cyclopropanes including *cis–trans* isomerization,[1] rearrangement to olefins and indans,[1a,2,3] and fragmentation to carbenes,[4] all presumably by homolytic mechanisms. We now wish to report the first unequivocal examples of a new photochemical reaction, the addition of protic compounds, YH, such as methanol, acetic acid, and water, to ordinary cyclopropanes I in *ionic* fashion to give substituted propanes II.



a, R = R′ = H; R″ = C_6H_5
b, R = R″ = H; R′ = C_6H_5
c, R = R′ = C_6H_5; R″ = H

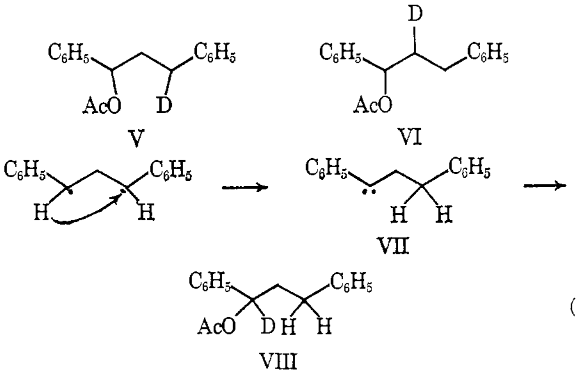
Y = OMe, OAc, or OH

When a 0.1 *M* solution of *trans*-1,2-diphenylcyclopropane (Ia)[5] in methanol was irradiated[6] the major product (40 ± 3%) was 1,3-diphenyl-1-propyl methyl ether (IIa, Y = OMe), $\nu_{\max}^{CS_2}$ 2815 (w) and 1100 (vs) (OMe), 1025 (m), 960 (m), 902 (m), 760 (s), 740 (vs), and 695 cm^{-1} (vs), identified by infrared, nmr, and elemental analysis and by independent synthesis.[7] Also present were benzyl methyl ether (III, Y = OMe; 2%) undoubtedly formed from phenylcarbene,[4] 1-phenylindan (IV; 12%), *cis*-1,2-diphenylcyclopropane (Ib; 2%), and Ia (6%).[1a,2] In the absence of light methanol did not react with 1,2-diphenylcyclopropane.



1,3-Diphenyl-1-propyl acetate (IIa, Y = OAc) was obtained (20% conversion) together with benzyl acetate (3%, from phenylcarbene) and other products when acetic acid was employed as the solvent. The transformation must be entirely photochemical since Ia was unaffected by heating to 190° in acetic acid for 23 hr. Acetate IIa (Y = OAc) was identical with a synthetic sample[8] in all respects, and its structure was consistent with its infrared ($\nu_{\max}^{CS_2}$ 1735 and 1230 cm^{-1}) and nmr spectra. The latter was distinguished by a triplet centered at τ^{CCl_4} 4.29 (one proton, *J* = 11 cps), singlets at τ 2.75 and 2.88 (five protons each), and a complex multiplet at τ 7.2–8.3 (seven protons).

Two possible pathways from I to IIa were excluded by examining the nmr spectrum of the acetate isolated from a similar irradiation in deuterioacetic acid. The infrared spectrum of the resulting acetate closely resembles that of IIa (Y = OAc) but possesses an additional peak at 2150 cm^{-1} (m) (C–D). The nmr spectrum exhibited a triplet (one proton) identical with that which characterizes the benzylic proton adjacent to oxygen in the undeuterated acetate. The presence of this triplet together with the decrease in relative area of the τ 7.2–8.3 multiplet to six protons forces the conclusion that deuterium addition occurred at C_3 as formulated in structure V. Preliminary mass spectral data are also compatible with this interpretation.

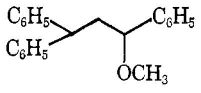


(1)

Thus, deuterioacetic acid did not react with 1,3-diphenylpropene (a known irradiation product of Ia[1a]), which would have given VI, nor with conceivable[9] carbene VII, the addition product of which would have been VIII (eq 1).

Irradiation of a supersaturated 0.1 *M* solution of Ia in an equimolar water–acetic acid mixture gave propanol IIa (Y = OH; *ca.* 12%),[10] identical with the alcohol obtained by reaction of hydrocinnamaldehyde with phenylmagnesium bromide; $\nu_{\max}^{CS_2}$ 3535, 3330, 1050, 905, 740, 695, and 530 cm^{-1}.

1,1,2-Triphenylcyclopropane (Ic) was irradiated in methanol to find out whether the methoxy group would add preferentially at the benzhydrylic carbon to give IIc or at the benzylic carbon to yield IX. The former



IX

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(1) (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.*, **87**, 1410 (1965); (b) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963).

(2) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Letters*, 2951 (1965).

(3) H. Kristinsson and G. W. Griffin, *ibid.*, 3259 (1966).

(4) H. Kristinsson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind.* (London), 1562 (1966).

(5) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952); R. M. Dodson and G. Klose, *Chem. Ind.* (London), 450 (1963); We thank Professor Dodson for generous samples of Ia and Ib with which this study was initiated. Ia containing 17% *cis* isomer Ib was used in most experiments.

(6) Unless stated otherwise, 0.1 *M* solutions in quartz tubes were carefully degassed and irradiated for 24 hr at 30° in a Rayonet chamber reactor (Southern New England Ultraviolet Company, Middletown, Conn.) equipped with 16 8-w low-pressure mercury lamps; products were isolated and yields determined by glpc on a 2 m × 0.6 cm i.d. silicone grease column using methyl laurate as an internal standard. No attempt was made to find optimum conditions.

(7) Prepared from III (R = OH) by a Williamson synthesis. *Cf.* A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 3723 (1953).

(8) L. F. Hewitt and J. Kenyon, *J. Chem. Soc.*, **127**, 1094 (1925).

(9) The hypothetical reaction leading to VIII is the reverse of the well-known hydrogen abstraction process known to occur with arylcarbenes; it has not yet been observed. See W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 86.

(10) A heavy precipitate formed on the walls during irradiation, and yields of IIa (Y = OH and OAc) were erratic.

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 [$\nu_{\max}^{\mathrm{CS_2}}$ 1745 (vs), 1240 (vs), 1215 cm^{-1} (vs)] and nmr [$\tau^{\mathrm{CDCl_3}}$ 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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[12] A. W. Fort and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 584 (1956).

[13] The formation of indan IV was quenched completely by air. The rearrangement of arylcyclopropanes to indans will be discussed in a later paper.

[14] R. C. Helgeson and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 509 (1966).

[15] P. J. Kropp, *ibid.*, **88**, 4091 (1966); J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).

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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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[1] This work was supported in part by a grant from the National Institutes of Health (GM-05830).

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[4] T. Higuchi and K.-H. Gensch, *J. Am. Chem. Soc.*, **88**, 3874 (1966).