

slightly outweigh attractive electronic correlation (London) forces amounting to about 2 kcal. per mole. It seems possible that, at the slightly greater bond distance existing in the transition state of the present reaction, the order of importance of these repulsive and attractive forces may be reversed.⁸ If so, we are provided with an explanation for the preferential formation of the less stable episulfone.

(6) London forces between atoms are believed to fall off with the reciprocal sixth power of the internuclear distance.⁶ Repulsive forces between atoms have been described by a function involving the reciprocal twelfth power of the distance (Lennard-Jones 6-12 potential).⁷

(7) J. O. Hirschfelder, C. F. Curtis and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 1070-1075.

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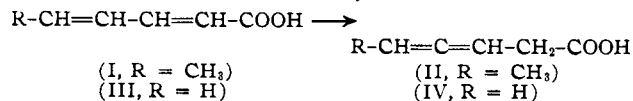
PHOTOCHEMICAL FORMATION OF ALLENES IN SOLUTION

Sir:

Srinivasan has reported¹ the vapor phase photoisomerization of 1,3-butadiene to 1,2-butadiene and of 1,3,5-hexatriene to 1,2,4-hexatriene. As part of an investigation of the extent of photochemical production of cyclobutenes,² systems containing dienes present in extendedly conjugated systems are being examined in this Laboratory. It is here reported that sorbic acid (I) and the homologous acid III, in dilute solution, are isomerized by light to the corresponding allenes, II and IV.

Irradiation³ of a 3% solution of sorbic acid in dry diethyl ether until almost no starting material remained (ultraviolet absorption) gave, after fractional distillation, the acid II (20%), b.p. 63° (0.4 mm.), m.p. 23°, n_D^{25} 1.4770. This product showed no ultraviolet maximum, but had ϵ 460 at 220 $m\mu$, ϵ 4200 at 192 $m\mu$ (in C_6H_{18}), while its infrared spectrum possessed the characteristic allene maximum at 1972 cm^{-1} ; its methyl ester (from diazomethane, n_D^{20} 1.4595) and its *p*-bromophenacyl ester (m.p. 68.5°) both showed this peak at 1972 cm^{-1} . The acid (II) in ethyl acetate, over Adams catalyst, absorbed two equivalents of hydrogen to yield caproic acid, and, on ozonolysis followed by oxidation of the ozonide with hydrogen peroxide in formic acid, gave malonic acid (76%). When heated with 10% aqueous sodium hydroxide⁴ at 70° during 15 min., the photoproduct was re-isomerized to sorbic acid (48%).

Irradiation of 2,4-pentadienoic acid (III)⁵ under similar conditions, followed by fractional distillation,



gave 3,4-pentadienoic acid (IV)⁴ in 32% yield. This product (m.p. 1.5°) was identified by its infrared maximum at 1965 cm^{-1} , by its low ultraviolet absorption, and by alkali catalyzed isomerization⁴ to the starting material (83%).

(1) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 5063 (1960); **83**, 2806 (1961).

(2) K. J. Crowley, *Proc. Chem. Soc.*, 334 (1962); cf. R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1962).

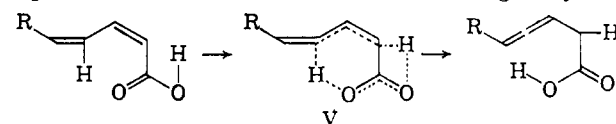
(3) A 450-watt Hanovia high-pressure mercury vapor lamp was used in a double walled water-cooled Vycor glass immersion well; rather more than 1 hr. irradiation was required per gram of sorbic acid. Non-allenic monomeric products were obtained in only minor amounts in all irradiations described.

(4) E. R. H. Jones, G. H. Whitham and M. C. Whiting, *J. Chem. Soc.*, 3201 (1954).

(5) E. P. Kohler and F. R. Butler, *ibid.*, **48**, 1041 (1926).

The yield of allene (II) was considerably increased and the irradiation time reduced by the addition of 1% of formic acid. No allene-type product was detected on irradiation of 5% aqueous potassium sorbate. Irradiation of a 1% solution of methyl sorbate in ether containing 10% formic acid resulted in an 8% yield of the methyl ester of II. This product could not be detected when the irradiation was carried out in the absence of formic acid, although a low (0.1%) yield of the allene ester was indicated when the concentration of methyl sorbate was increased to 5%.

Thus the non-ionized carboxyl group appears to play a part in the isomerization, so that the change may take



place as generalized in V, after preliminary conversion to the 2,3-*cis* isomer. The mechanism and the possibility of extending this reaction are being investigated.

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AN INVERSE CARBON ISOTOPE EFFECT ON THE IONIZATION OF TRIPHENYLMETHYL CHLORIDE. KINETIC ISOTOPE EFFECTS ON SN1 AND SN2 REACTIONS¹

Sir:

The carbon kinetic isotope effect on bimolecular nucleophilic substitution in methyl halides (SN2 reaction) is known to be large: reported C¹²:C¹³ rate ratios at 25° range from 1.04 to 1.09² and C¹²:C¹⁴ ratios are correspondingly higher.³ In contrast to this, the only reported carbon isotope effect on unimolecular heterolysis of a carbon-halogen bond (SN1 reaction) is small. The C¹²:C¹⁴ rate ratio for the solvolysis of *t*-butyl chloride at 25° is 1.027,⁴ this corresponds to a carbon-13 isotope effect of just over 1.01. We wish to report an isotope effect on an equilibrium closely related to SN1 heterolysis which supports this low rate ratio: the C¹²:C¹³ equilibrium constant ratio for the ionization of triphenylmethyl chloride in liquid sulfur dioxide at 0° is 0.983. Analysis of this system suggests that carbon isotope effects on SN1 reactions may in general be smaller than those on SN2 reactions.

The isotope effect on this ionization was measured by comparing the conductances of sulfur dioxide solutions of triphenylmethyl chloride and triphenylmethyl- α -C¹³ chloride. The labeled material was prepared from barium carbonate-C¹³ with a nominal carbon-13 content of 66%. This carbonate was converted to benzoic- α -C¹³ acid. The acid, *via* its ester, was transformed to triphenylmethanol- α -C¹³ and the chloride was obtained directly from this alcohol. The carbon-13 content of the chloride and of two of its precursors was 65.6 atom % at the labeled position (direct analysis). The ratio of ionization constants in liquid sulfur dioxide solution at 0° was determined by measuring conductivities of separate solutions of normal and isotopic chlorides at very nearly the same concentrations.⁵

(1) Research supported in part by the U. S. Atomic Energy Commission under USAEC Contract AT(11-1)-1025 to the Illinois Institute of Technology and at Brookhaven National Laboratory.

(2) K. R. Lynn and P. E. Yankwich, *J. Am. Chem. Soc.*, **83**, 53, 790, 3220 (1961).

(3) M. L. Bender and D. F. Hoeg, *ibid.*, **79**, 5649 (1957); G. J. Buist and M. L. Bender, *ibid.*, **80**, 4308 (1958).

(4) M. L. Bender and G. J. Buist, *ibid.*, **80**, 4304 (1958).

(5) See N. N. Lichtin, E. S. Lewis, E. Price and R. R. Johnson, *ibid.*, **81**, 4520 (1959), for the basic principles of the method.