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.[6] 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.[5] 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 reported[1] 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.

Irradiation[3] 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°, $n^{23}D$ 1.4770. This product showed no ultraviolet maximum, but had ϵ 460 at 220 mμ, ϵ 4200 at 192 mμ (in C_8H_{18}), while its infrared spectrum possessed the characteristic allene maximum at 1972 cm.$^{-1}$; its methyl ester (from diazomethane, $n^{20}D$ 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 hydroxide[4] 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,

R-CH=CH-CH=CH-COOH ⟶

	R-CH=C=CH-CH₂-COOH
(I, R = CH₃)	(II, R = CH₃)
(III, R = H)	(IV, R = H)
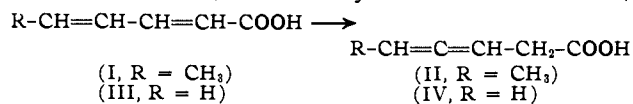
gave 3,4-pentadienoic acid (IV)[4] in 32% yield. This product (m.p. 1.5°) was identified by its infrared maximum at 1965 cm.$^{-1}$, by its low ultraviolet absorption, and by alkali catalyzed isomerization[4] to the starting material (83%).

(1) R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 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
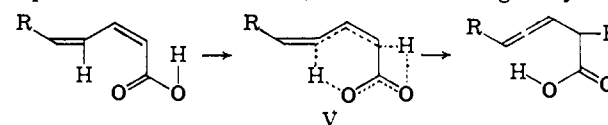
place as generalized in V, after preliminary conversion to the 2,3-*cis* isomer. The mechanism and the possibility of extending this reaction are being investigated.

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AN INVERSE CARBON ISOTOPE EFFECT ON THE IONIZATION OF TRIPHENYLMETHYL CHLORIDE. KINETIC ISOTOPE EFFECTS ON SN1 AND SN2 REACTIONS[1]

Sir:

The carbon kinetic isotope effect on bimolecular nucleophilic substitution in methyl halides (SN2 reaction) is known to be large: reported $C^{12}:C^{13}$ rate ratios at 25° range from 1.04 to 1.09[2] and $C^{12}:C^{14}$ 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 $C^{12}:C^{14}$ 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 $C^{12}:C^{13}$ 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-C^{13} chloride. The labeled material was prepared from barium carbonate-C^{13} with a nominal carbon-13 content of 66%. This carbonate was converted to benzoic-α-C^{13} acid. The acid, *via* its ester, was transformed to triphenylmethanol-α-C^{13} 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.

Two different preparations of each chloride were used and three different types of conductivity cells were employed. The average of ionization constants for 22 determinations was 0.9890, $\sigma = 0.0021$,[6] (σ is standard deviation of mean value) which corresponds to an isotope effect (K_{12}/K_{13}) of 0.9833, $\sigma = 0.0031$, for the completely labeled substance.

The probable source of this inverse isotope effect can be deduced by considering the mechanical properties of the chemical species involved in the ionization of triphenylmethyl chloride. The isotope effect can be expressed in the usual way as a ratio of partition functions and differences in zero-point energy for the isotopically substituted reactants and products. This reduces to an expression consisting of symmetry numbers, s, molecular masses, M, moments of inertia, A, B, C, and vibrational frequencies, ω ($u = hc\omega/kT$)

$$\frac{K_{12}}{K_{13}} = \left(\frac{s_{12}}{s_{13}}\right)_R\left(\frac{s_{13}}{s_{12}}\right)_P\left(\frac{M_{12}}{M_{13}}\right)_R^{1/2}\left(\frac{M_{12}}{M_{13}}\right)_P^{1/2} \times$$
$$\left(\frac{A_{13}B_{13}C_{13}}{A_{12}B_{12}C_{12}}\right)_R^{1/2}\left(\frac{A_{12}B_{12}C_{12}}{A_{13}B_{13}C_{13}}\right)_P^{1/2}\prod_i^{3n-6}\left(\frac{\sinh u_i(12)/2}{\sinh u_i(13)/2}\right)_R \times$$
$$\prod_i^{3n-6}\left(\frac{\sinh u_i(13)/2}{\sinh u_i(12)/2}\right)_P \quad (1)$$

Isotopic substitution does not alter the symmetry of either reactant or product, and the product of the symmetry number ratios is unity. The mass ratios contribute a factor of 0.9992 to the isotope effect. The moments of inertia of the product are not affected by isotopic substitution: the product is a symmetrical carbonium ion in which isotopic change is made at the center of mass. One of the principal moments of inertia of the reactant is also non-isotopic; the other two contribute a factor of 1.0003. This is for a triphenylmethyl chloride molecule with regular tetrahedral bonds about the central carbon atom and normal bond angles and bond lengths elsewhere. Use of any other reasonable model will not produce a significant change in this number. The combined effect of these terms of eq. 1—the non-vibrational component of the isotope effect—is a factor of 0.9995. This accounts for only 5% of the observed effect. Essentially all of this isotope effect therefore must be due to differences in vibrational frequencies.

Triphenyl carbonium ion has one atom and three vibrational degrees of freedom less than triphenylmethyl chloride. The observed inverse isotope effect, however, demands that the sum of the vibrational frequencies of the normal modes in the carbonium ion be greater than the sum for the chloride. Some vibrations in the ion, then, must be tighter than corresponding ones in the chloride by an amount sufficient to offset the effect of fewer vibrations, and the carbonium ion must have some bonds which are stronger than corresponding bonds in the chloride. An X-ray diffraction investigation of the structure of triphenylmethyl perchlorate shows that the carbon–phenyl bond in the carbonium ion is indeed 0.10 Å. shorter than the normal carbon–carbon single bond distance.[7] Badger's rule[8] predicts that the force constant of this shortened bond will be some 40% larger than the force constant of the carbon–phenyl bond in triphenylmethyl chloride. The effect of this increase in force constant on the vibrational frequencies is difficult to assess quantitatively, because vibrations of a molecule as complex as those being considered here cannot be treated as stretching and bending modes of single bonds. The frequencies of

(6) This value was obtained by weighting the mean ratios determined in each of the three types of cells in proportion to the reciprocals of the squares of their standard deviations: 0.9876, $\sigma = 0.0061$ ($n = 6$); 0.9866, $\sigma = 0.0043$ ($n = 8$); and 0.9901, $\sigma = 0.0026$ ($n = 8$).

(7) K. Eriks and A. Gomez de Mesquita, personal communication.

(8) R. M. Badger, J. Chem. Phys., 2, 128 (1934).

a number of normal modes will be changed, and a quantitative estimate of these changes requires a complete vibrational analysis. Changes large enough to account for the observed isotope effect of 1.7% are reasonable, however, by analogy with the equilibrium dissociation of the boron trifluoride–dimethyl ether complex. An inverse isotope effect of 3% (B^{10}/B^{11}) in this system has been attributed to vibrational changes accompanying a shortening of the boron–fluorine bond from 1.43 Å. in the complex to 1.295 Å. in boron trifluoride.[9]

This analysis suggests that the principle source of the inverse isotope effect of 1.7% on the ionization of triphenylmethyl chloride is the increased strength of carbon–phenyl bonds in the triphenyl carbonium ion. Isotopic substitution, occuring as it does near the center of a large molecule, has very little effect on molecular masses and moments of inertia. In an SN1 reaction these non-vibrational contributions to the isotope effect are also likely to be small: pure SN1 reactions have not been realized with very small molecules. SN1 reactions are, moreover, most common in systems where some stabilization of the intermediate carbonium ion is possible, and this usually takes the form of resonance stabilization of the positive charge. Such charge delocalization strengthens the bonds to the reacting carbon which are not being broken, and this strengthening offsets the loss in bonding produced by bond-breaking. Thus, in the solvolysis of t-butyl chloride, hyperconjugation strengthens the carbon–methyl bonds in the forming carbonium ion. This effect is not, of course, as large as that in the triphenyl carbonium ion, but it is enough to reduce the vibrational contribution to the isotope effect. The combination of these effects, a vanishing contribution from the non-vibrational parts of the isotope effect and a diminished vibrational contribution serves to produce a small isotope effect in those systems where SN1 reactions are most likely.

Acknowledgment.—We are grateful to Dr. R. E. Weston for many clarifying discussions.

(9) A. A. Palko, G. M. Begun and L. Landau, ibid., 37, 552 (1962).

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THE RADIATION INDUCED cis–trans ISOMERIZATION OF BUTENE-2

Sir:

The precise roles of electronic energy transfer, free radical reactions and charge or electron transfer in radiolyses are still uncertain. Van Dusen and Hamill[1] have pointed out that scintillation experiments demonstrate that singlet states are chemically unimportant in energy transfer processes induced by ionizing radiation. The possibility of triplet participation remains, but spectroscopic or other conclusive evidence has been lacking.

Olefins are very effective quenchers of the triplet state of benzene[2] and if pure cis- or trans-butene-2 is used for this purpose, isomerization results from the process

cis (or trans)-butene-2 + benzene* (triplet) ⟶
　　　　　　　　　　　　　　　butene-2* (triplet) + benzene
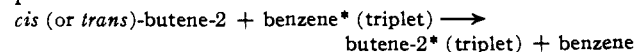
(1) W. Van Dusen and W. H. Hamill, J. Am. Chem. Soc., 84, 3648 (1962).

(2) R. B. Cundall and D. G. Milne, ibid., 83, 3902 (1961).