

Fig. 1.—Experimental and calculated spectra for potassium 2,2-dimethyldioxolane 5-carboxylate: spectrum A was measured on a 15% solution in deuterium oxide at 24.3 Mcps. Spectra B, C and D were calculated using the parameters shown. A and C transitions are represented by solid lines, B transitions are represented by dashed lines,

and combination transitions by solid lines with the vertical bar. It should be noted that in A the two barely resolved transitions from nucleus C have intensities the opposite of that predicted in B. This discrepancy results from lack of sufficient recorder response, since the spectrum obtained by sweeping downfield gave a spectrum in which the intensities were reversed and in agreement with B.

that of the carboxylate salt, provides further confirmation of this conclusion. The spectrum of this compound at 24.3 Mcps. agreed to less than 0.2 cps. in line position with that predicted from the set of parameters with  $A_{BC}$  negative, which was obtained from the 60 Mcps. spectrum. There was no apparent disagreement in intensity. The other three sets of parameters gave predictions obviously in error, that is, greater than 500% in intensity and 1 cps. in line position. The theoretical spectra of the remaining four compounds measured at 60 Mcps. also agree best with the observed spectra when  $A_{BC}$  is negative. The generality of these findings is being investigated.

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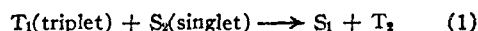
#### THE DETECTION OF TRIPLET STATES BY THE *CIS-TRANS* ISOMERIZATION OF BUTENE-2

Sir:

Hammond, Leermakers and Turro<sup>1</sup> have suggested that it is possible to study the mechanism of various photochemical reactions by effecting the production of triplet intermediates from the reactants by using benzophenone, and other similar triplets, produced by photoexcitation as sensitizers.

As a means of elucidating reaction mechanisms the method suffers from the disadvantage that although the mechanism of the photosensitized reaction may be correctly understood, it does not of necessity follow that the same, or similar, mechanism applies to the unsensitized reaction.

A more reliable method would be to use a system in which the induced triplet intermediate of the original reaction undergoes an exchange in multiplicity with some other added species in accordance with the expression



If a triplet intermediate is involved, this should suppress the reaction if the second triplet  $T_2$  is comparatively unreactive. This type of transition should occur readily if the O-O transition,  $T_1 \rightarrow T_2$ , is exothermic. Usually, such interchanges can only be followed by phosphorescence or spectroscopic measurements.

The *cis-trans* isomerization of butene-2 through the triplet state provides a straightforward chemical means of following such excitation interchanges. Photosensitization studies in the vapor phase using mercury,<sup>2</sup> sulfur dioxide,<sup>2</sup> benzene<sup>2,3</sup> and a variety of other organic photosensitizers have shown that

(1) G. S. Hammond, P. A. Leermakers and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2395 (1961).

(2) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

(3) R. B. Cundall and D. G. Milne, to be published.

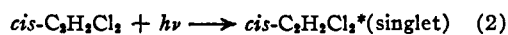
an exchange of multiplicity, resulting in the possibility of isomerization, can be accomplished if the photosensitizing species has energy in excess of approximately 60 kcal. mole<sup>-1</sup> above its ground state. If this latter condition is satisfied reaction (1) occurs at every collision. Deactivation of the butene-2 triplet produces *cis* and *trans* isomers with equal probability. By using one of the pure isomers and only working with low percentage conversions, it is possible to say that the number of molecules of butene-2 which have been isomerized is one half the number of triplet molecules which undergo the interchange. Accurate estimation of triplet state production is, therefore, possible.

Butene-2 has the advantage that it does not itself absorb light of wave length greater than 2000 Å., the normal photochemical range.

Two examples of systems which we have examined by this method are the direct photochemical decomposition of formic acid and the photochemical isomerization of *cis*-dichloroethylene.

The decomposition of formic acid (20 mm.) into hydrogen, carbon monoxide, carbon dioxide and water was quenched by pressures of *cis*-butene-2 up to 134 mm. In the process, isomerization of *cis*-butene-2 occurred. This shows that a triplet state is involved in the photolysis of formic acid.

The *cis-trans* rearrangement of *cis*-dichloroethylene (15 mm.) is also quenched by butene-2, but without any isomerization of butene-2 at pressures of 120 mm. At lower butene-2 pressures some isomerization did occur. This may be explained by the scheme



At high butene-2 pressures the excited singlet state is deactivated before transition to the triplet can occur. This aspect of the reaction would not have been apparent using the method of Hammond, Leermakers and Turro.

Triplet butene-2 molecules do not isomerize other molecules of butene-2. This combined with the fact that no evidence of reactivity of such species has been found suggests that they are deactivated readily to vibrationally excited ground states by crossing of the potential energy surfaces.<sup>4</sup> The technique may be extended to studies in solution.

(4) W. J. Potts, Jr., *J. Chem. Phys.*, **23**, 65 (1955).

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#### TIN-PROTON SPIN-SPIN COUPLING IN METHYL TIN HALIDES AND RELATED COMPOUNDS

Sir:

Because of recent interest<sup>1</sup> in the configuration and nature of bonding in alkyltin cations and related compounds, we wish to communicate some n.m.r. measurements of indirect tin-proton spin-spin coupling constants in a series of methyltin chlorides. We interpret our results as having a direct

(1) (a) E. G. Rochow, *XVII Internat. Congress Pure and Appl. Chem.*, **1**, 136 (1959); (b) R. Okawara, D. E. Webster and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3287 (1960); (c) R. Okawara and H. Sato, *J. Inorg. Nuclear Chem.*, **18**, 204 (1961).

bearing on the nature of hybridization of the tin atom in the compounds studied here.

The first reports<sup>2</sup> of the proton magnetic resonance spectra of methyl derivatives of Group IVb elements have dealt solely with the single sharp, strong absorption that arises from methyl protons, and of its variation in chemical shift with respect to substitution and electronegativity of the central atom. More recently, brief mention has been made<sup>3</sup> of tin-proton coupling observed for dimethyltin dichloride in water and acetone solutions, and for tetramethyltin, from the measured line separations in <sup>119</sup>Sn n.m.r. spectra.

We have measured<sup>4</sup> the doublet-satellite resonances appearing at relative intensity of 3-4% of the main peak, in a number of methyl derivatives of tin. These doublets arise from the coupling of methyl protons with naturally occurring isotopes <sup>117</sup>Sn and <sup>119</sup>Sn (both with *I* = 1/2; relative abundances 7.67 and 8.68%, respectively). Results are presented in Table I.

TABLE I

Compound <sup>a</sup>	T, °C.	Coupling Constants (c.p.s.) <sup>b</sup>	
		<sup>117</sup> Sn-CH <sub>3</sub>	<sup>119</sup> Sn-CH <sub>3</sub>
(CH <sub>3</sub> ) <sub>4</sub> Sn	31	51.5	54.0
51% CCl <sub>4</sub>	31	51.4	53.8
5% CCl <sub>4</sub>	31	51.6	53.7
(b)			54
(CH <sub>3</sub> ) <sub>3</sub> SnCl	40	57.4	59.7
38% CCl <sub>4</sub>	31	56.0	58.5
62% C <sub>6</sub> H <sub>6</sub>	31	56.5	59.2
56% H <sub>2</sub> O	31	65.2	68.4
(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>	110	68.0	71.0
satd. < 14% CCl <sub>4</sub>	31	66.6	69.7
47% H <sub>2</sub> O	31	97.4	101.9
(b)			98
CH <sub>3</sub> SnCl <sub>3</sub>	55	95.7	100.0
46% CCl <sub>4</sub>	31	95.3	99.5
51% C <sub>6</sub> H <sub>6</sub>	31	95.4	99.9
49% H <sub>2</sub> O	31	125.4	131.1

<sup>a</sup> Compounds first listed as neat liquids, then as per cent. by weight in solution of various solvents. <sup>b</sup> Data from ref. 3. <sup>c</sup> Values are given to a precision of ±0.5%.

Ramsey,<sup>5</sup> Karplus and Anderson<sup>6</sup> and others have shown that the Fermi contact contribution to the spin-spin coupling constant *A*<sub>N'</sub> between two nuclei is directly proportional to the product ρ(O)<sub>N</sub>ρ(O)<sub>N'</sub> of the electron densities of the two bonding orbitals, through which they interact, at their respective nuclei. For covalently bonded hydrogen, ρ(O)<sub>H</sub> usually is considered to be the same as that for the hydrogen atom in the 1s state. For other atoms, in particular those with hybridized bonding orbitals, a simple LCAO treatment predicts that ρ(O)<sub>N</sub> is proportional to the per cent. s-character in the hybridized atomic orbital used in forming the

(2) (a) A. L. Allred and E. G. Rochow, *ibid.*, **5**, 269 (1958); (b) M. P. Brown and D. E. Webster, *J. Phys. Chem.*, **64**, 698 (1960).

(3) J. J. Burke and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 326 (1961).

(4) Proton resonances were observed at 40 Mc. using a Varian V-4300 B spectrometer. Frequency measurements were made by the side-band method using a calibrated Hewlett-Packard Model 200D audiofrequency oscillator.

(5) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

(6) M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **30**, 6 (1959).