trum are much broader than those of the ClF_4 spectrum in Figure 1. The broadening appears to be uniform for the different components and therefore is not attributable to a modulation of the spin distribution (on the ESR time scale) nor to anisotropic broadening resulting from incomplete tumbling of the ClF_6 radical. It is conceivable that the broadening is caused by enhanced spin-lattice relaxation through a mechanism of spin-orbit coupling.[12] Such a mechanism might well be operative if there is a mixing of the $(a^*_{1g})^1$ ground state configuration with the orbitally degenerate $(a^*_{1g})^0\ (t^*_{1u})^1$ excited state during the course of deformations about a mean of octahedral geometry. A pseudo-Jahn-Teller effect of this type has been discussed[2a] in the analogous case of XeF_6.

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References and Notes

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(8) (a) J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 3112 (1973). (b) Also, an intense ESR spectrum of ClF_4 was observed after γ irradiation of SF_6 containing chlorine trifluoride. This method of generation differs from that used by Morton and Preston[8a] and thereby confirms their identification of the ClF_4 radical.

(9) The absence of a central septet spectrum with 500-fold greater intensity rules out the possibility that the quartet of septets is due to ^{33}S ($I = {}^3/_2$) satellites in natural abundance. Also, the spectrum reported in this paper is clearly different from a weak spectrum noted previously[5] for a radical with six equivalent fluorines and thought to be SF_6^-. The latter spectrum ($a(^{19}F) = 195$ G; $g = 2.006$) possessing well-resolved second-order fluorine splittings has been also observed in our studies of γ-irradiated SF_6 without additives.

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A Photochemical Rearrangement without Light. Dioxetane Effected Photochemistry by Direct Intramolecular Excitation[1]

Sir:

The term "photochemistry without light" was coined[2] in regard to experiments designed to place a molecule midway on the hypersurface leading from excited state reactant to ground state product by indirect generation of photochemical species[2] (e.g., zwitterionic). A second type of photochemistry without light begins with the excited state itself, this generated by intermolecular energy transfer from dioxetane derived sensitizer.[3]

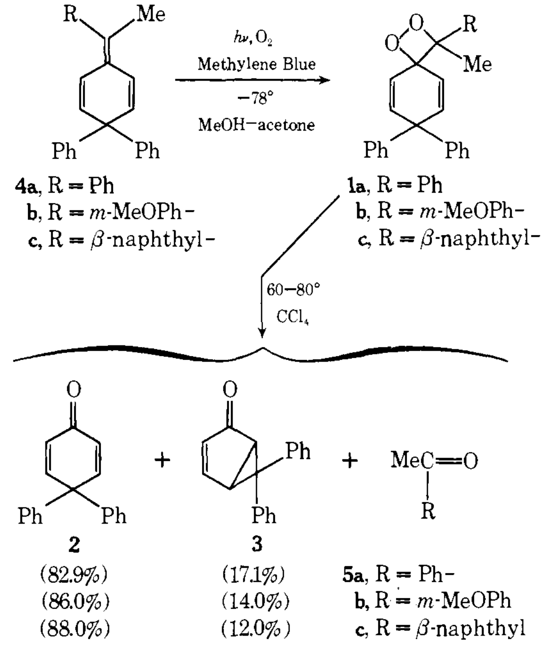
Thus there are two versions of photochemistry without light. That starting with excited state might be termed "vertical" and that placing a molecule on the photochemical reaction coordinate at a later stage could be termed "nonvertical".

Recently, an example of a very novel type of vertical photochemistry without light was reported by Foote.[4] Here the reacting ketonic moiety was incorporated in the initial dioxetane and no energy transfer step was involved. Foote noted referee criticism that an alternative, nonexcited state, free-radical mechanism could account for his reaction products, but he provided evidence against this alternative.

The present communication reports the following. (a) The synthesis of a series of dioxetanes (**1a–c**) which are formal adducts of 4,4-diphenylcyclohexadienone (**2**) and a series of ketones. (b) The thermal decomposition of these to give 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**3**) in the Type A rearrangement characteristic of the photochemistry of this dienone.[5] This provides the first example of a skeletal rearrangement of an excited state generated directly, without intermolecular energy transfer. Here free-radical alternatives do not apply. (c) Direct determination of the efficiency of excited state formation. (d) Efficiencies remarkably independent of the energy and configuration of excited states available to the second ketonic fragment. (e) Direct generation of n-π^* triplet 4,4-diphenylcyclohexadienone and observation of its behavior.

The desired dioxetanes (**1a–c**) were obtained from the reaction of singlet oxygen with the exocyclic double bond of the corresponding 1-methylene-4,4-diphenyl-2,5-cyclohexadienes[6] (**4a–c**) (note Chart I). The dioxetanes were isolated by chromatography at −20°. Crystallization proved effective in two cases to give mp 88–92° dec for methyl phenyl dioxetane **1a** and mp 89–94° dec for methyl β-naphthyl dioxetane **1c**.

Chart I. Preparation and Reaction of Dioxetanes



These dioxetanes were decomposed thermally between 60 and 80°.[7] The products obtained in each of the three cases proved to be 4,4-diphenylcyclohexadienone (**2**), 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**3**), and the corresponding methyl ketone (i.e., acetophenone, *m*-methoxyacetophenone, or β-acetonaphthone). Note Chart I.

Since the efficiency of formation of 6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one (**3**) starting with either singlet or triplet 4,4-diphenylcyclohexadienone (**2**) is known[5b] to be 0.86 (i.e., $\phi_{isc} = 1$), we calculate the efficiency of generation of excited dienone to be (1/0.86) times the 17.1, 14.0, and 12.0% yields of bicyclic ketone **3** derived from the three dioxetanes, respectively. The literature[8,9] provides support for the excited states generated to be heavily $n-\pi^*$ triplets.

With this in mind, we find it remarkable that the efficiency of the Type A rearrangement is so slightly dependent on the dioxetane reactant structure, or, equivalently, on the second ketonic product (i.e., **5a**, **5b**, or **5c**) generated. In particular, one might have expected that in the case of β-acetonaphthone formation from the β-naphthyl dioxetane **1c**, the reaction transition state would sense the availability of a low (i.e., 59 kcal/mol) β-acetonaphthone triplet and would avoid generating the 68.5 kcal/mol 4,4-diphenylcyclohexadienone triplet. This is *not* the case.[10]

We can conclude that the dioxetane decomposition is controlled by the energetics leading to $n-\pi^*$ excited species. Here we have experimental evidence in support of literature theoretical suggestions[9] for preferential generation of the $n-\pi^*$ triplet. Our observation of the system's inability to generate β-acetonaphthone $\pi-\pi^*$ triplets suggests that dienone $\pi-\pi^*$ triplets are similarly inaccessible. The lack of energy drainage to the 59 kcal/mol β-acetonaphthone triplet implies a lack of inter- and intramolecular equilibration between the states of dienone and β-acetonaphthone. The nonequilibration between dienone $n-\pi^*$ and $\pi-\pi^*$ configurations has independently been advanced by Schuster.[12a] Considering the extreme rapidity of the rearrangement of 4,4-diphenylcyclohexadienone triplet,[5b] these conclusions seem reasonable.

Thus, $n-\pi^*$ triplet 4,4-diphenylcyclohexadienone, when generated specifically, gives the usual Type A rearrangement. Although this configurational assignment is somewhat controversial,[12b] our conclusion is in agreement with the postulate we made many years ago.[5a]

The 4,4-diphenylcyclohexadienone system has proven unique in that both vertical and nonvertical photochemistry without light have been accessible. Thus we have now been able to place a molecule both midway on the hypersurface leading from excited state to product and also at the origin corresponding to initial excited state itself.

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(6) Synthetic and experimental detail will be reported in our full paper. Satisfactory elemental analyses were obtained on all thermally stable compounds and spectral data were used for the dioxetanes.

(7) The unimolecular rate of cleavage of methyl phenyl dioxetane **1a** at 71.4° was determined by NMR following to be 4.5×10^{-4} sec^{-1} (CCl_4). This is remarkably similar to the reported[8a] rate of 4.0×10^{-4} sec^{-1} (70°, benzene) for 3,3,4,4-tetramethyl-1,2-dioxetane.

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(9) A variety of theoretical considerations predict formation of $n-\pi^*$ triplet products: (a) D. Kearns, *Chem. Rev.*, **71**, 345 (1971); (b) D. R. Roberts, *J. Chem. Soc., Chem. Commun.*, 683 (1974); (c) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 7578 (1974); (d) M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, *ibid.*, **96**, 7579 (1974).

(10) Reaction of β-naphthyl dioxetane **4c** in the presence of 0.10 *M* cyclohexadiene triplet scavenger led to no diminution of bicyclic ketone product, establishing absence of complicating chain processes and free β-acetonaphthone triplet.

(11) The mirror image situation has been reported by N. J. Turro, G. Schuster, J. Pouliquen, R. Pettit, and C. Mauldin, *J. Am. Chem. Soc.*, **96**, 6797 (1974), who concluded that $\pi-\pi^*$ triplet excitation generated from Dewar acetophenone was not readily convertible to $n-\pi^*$ excitation.

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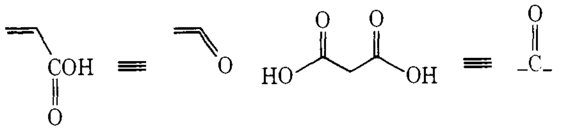
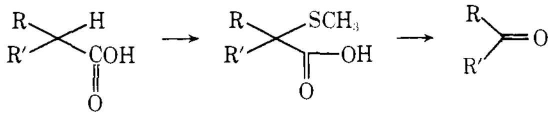
New Synthetic Reactions. Oxidative Decarboxylation

Sir:

The conversion of a carboxylic acid (or derivative) to a ketone with loss of one carbon atom plays an important role in organic chemistry.[1] This degradation is an important tool in the structural elucidation of natural products.[2] It also allows carboxylic acid derivatives to serve as synthetic equivalents of other structural fragments. For example, acrylic acid becomes an equivalent of ketene,[3] carboxylic acids become acyl anion equivalents, and malonic acid becomes an equivalent of a carbonyl dianion. We wish to report a particularly convenient new two-step method (see eq 1) which utilizes a novel oxidative decarboxylation as the key step.[4]





(1)

1

The sulfenylation of the dianions of carboxylic acids[5] generated utilizing 2 equiv of lithium diisopropylamide followed by addition of dimethyl disulfide proceeds practically quantitatively.[6] For dialkylcarboxylic acids (i.e., **1**, R and R′ are alkyl), addition of HMPA for the metalation and sulfenylation is recommended.

To a mixture of the sulfenylated acid and sodium bicarbonate in alcohol solution (methanol, ethanol, or *tert*-butyl alcohol) is added solid *N*-chlorosuccinimide at room temperature. Gas evolution (carbon dioxide) occurs immediately. Aqueous work-up allows isolation of the initial product, the ketal, which is readily hydrolyzed to the ketone with aqueous hydrochloric acid. Table I summarizes various applications. The yields have not been optimized in any case. Successful results have been obtained with an α,α-diaryl, an aryl alkyl, and dialkyl carboxylic acids. It is interesting to note that a double bond (entries 3 and 6) and a ketone (entry 5) do not interfere in the oxidative elimination step. Entry 5 demonstrates the availability of the requisite intermediate by hydrolysis of the sulfenylated ester.[6a,c] However, the stringent conditions required for such a hydrolysis makes it much less attractive than the direct sulfenylation of the acid.

The accompanying equations provide a mechanistic rationale for the oxidative decarboxylation. Chlorination at