Table I. Photosensitized Isomerization of Stilbene with Benzophenone in the Presence of Isoprene

trans-Stilbene, *M*	Isoprene, *M*	ϕ_{obsd} (*trans*→*cis*)[a]	$\phi_{predicted}$
0.056	0	0.55[b]	0.56[d]
0.045	0.108	0.23_1[c]	0.173[e]
0.045	0.52	0.10_6[c]	0.0475[e]
0.045	1.05	0.084[c]	0.0242[e]
0.045	5.2	0.045_4[c]	0.0050[e]
0.022	3.0	0.025_8[c]	0.0043[e]

[a] Experiments were performed at 3660 A in benzene solvent. Gas chromatographic analyses were reproducible to ±3%. Conversion was roughly 4–6% in general and never over 12%. [b] Conventional ferrioxalate actinometry. [c] Actinometry *via* unquenched samples which were irradiated either in parallel or both before and after, corrected for back-reaction by the method of Hammond and Lamola (*J. Chem. Phys.*, **43**, 2129 (1965)). [d] H. A. Hammond, D. E. DeMeyer, and J. L. R. Williams, *J. Amer. Chem. Soc.*, **91**, 5180 (1969). [e] $\phi_{predicted} = 0.59 \times$ stilbene molarity/(stilbene molarty + isoprene molarity); $0.59 = k_2/(k_1 + k_2)$ from ref 1.

filter. The only apparent explanation is that *isoprene triplets must be capable of transferring excitation to the stilbenes.*[9] The magnitude of the effect is such that, at 1 *M* isoprene, about 12% of the isoprene triplets transfer excitation to 0.05 *M* *trans*-stilbene ($E_T = 50$) and about 3% transfer excitation to 0.05 *M* *cis*-stilbene ($E_T = 57$). It is not surprising that Saltiel's study[3] detected no excitation transfer with hexadiene.

For $k_c = k_t = k_I$ and $k_2 = 1.43k_1$,[1] we calculate that $k_D/k_{t\text{-}I} = 0.32 \pm 0.04$ *M* and $k_B/k_{t\text{-}I} = 0.06 \pm 0.02$ *M*, from the data in Table I. Our best estimates from comparable data starting with *cis* are *ca.* 2 ± 1 *M* for $k_D/k_{c\text{-}I}$ and 0.2 ± 0.1 for $k_B/k_{c\text{-}I}$. The $\phi_{t\rightarrow c}$ data indicate $k_D/k_B = 6 \pm 2$ *M*, in fair agreement with the value of 16 *M* obtained by Liu, Turro, and Hammond.[2] Quantitative comparison of our results and those for azulene quenching of isoprene triplets[2] ($k_{Az}/k_B = 1200$) indicate that *trans*-stilbene is much less efficient than azulene in quenching isoprene triplets. Despite the fact that the reaction is some 10 kcal/mol exothermic (based on the spectroscopic triplet energies), *trans*-stilbene quenches isoprene triplets *at least some two orders of magnitude less than diffusion controlled.*

The obvious explanation for the slowness of this rate, that isoprene triplets are nonvertical[1,2] and therefore not subject to expectations based on conventional triplet excitation donors, is surely right in general but does not probe the nature of this donor–acceptor interaction. Two reasonable possibilities come to mind: (1) excitation transfer is accomplished relatively efficiently from the small amount of spectroscopic triplet in thermal equilibrium with the remainder of the isoprene triplet molecules, or (2) deexcitation occurs from a nonvertical geometry. Our results indicate the latter explanation. The spectroscopically accessible isoprene triplet at 60 kcal should behave essentially like any other donor triplet of comparable energy in its k_t/k_c ratio, *i.e.*, the excitation ratio for the stilbene isomers. That ratio is 1.6 for several sensitizers of $E_T = 59.5 \pm 0.3$ kcal.[1] The quantum yield data given above indicate a rough value of ~5 for isoprene triplets. A much more precise value of 4 ± 0.5 may be obtained by analysis of the photostationary state data *via* eq 12 and the parameters derived from eq 11. This ratio is clearly not characteristic of a 60-kcal triplet.

Adroit application of the techniques we describe should ultimately provide a wealth of revealing data on the nature of bimolecular deactivation of nonvertical triplets.

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[9] We rule out the possibility that the triplet isoprene–stilbene interaction responsible for isomerization is biradical in nature, since such a process would be expected to favor production of *trans*-stilbene rather than *cis*; *cf.* ref 7a, among other recent references to photochemically generated biradicals.

Chemiluminescence from the Reaction of Ketenes, Singlet Oxygen, and Fluorescers

Sir:

We find that reactions of certain ketenes and ketene acetals with singlet oxygen and fluorescers (Flr) produce chemiluminescent light emission. Bright light emission occurs when solutions of ketene or diphenylketene and triphenyl phosphite ozonide[1] in methylene chloride are mixed at −70° and allowed to warm to room temperature in the presence of 9,10-bis(phenylethynyl)anthracene (BPEA) or 9,10-diphenylanthracene (DPA). The reaction of diphenylketene glycol acetal produces a very weak light emission and tetraphenylethylene fails to react under these conditions.

The spectrum of chemiluminescent light emission from the diphenylketene reaction is identical with the fluorescence of BPEA, the fluorescer used. The chemiluminescent quantum yields were measured and are summarized in Table I. The quantum yield based on diphenylketene is 1.9×10^{-4} einstein mol^{-1} and decreases slightly with increasing concentration of diphenylketene. The quantum yield decreases more strongly with decreasing BPEA concentration. Although some of the fluorescer may react with singlet oxygen to form an *endo*-peroxide, a possible decomposition of that *endo*-peroxide is not responsible for the light emission since 9,10-diphenylanthracene *endo*-peroxide is stable under the reaction conditions.

Table I. Chemiluminescent Emission from the Reaction of Diphenylketene and Singlet Oxygen

Diphenylketene, $10^2 \times$ mol l.$^{-1}$	BPEA, mol l.$^{-1}$	Quantum yield, einstein mol^{-1} $\times 10^{-4}$
0.463	1×10^{-3} + 0.01 g of solid	1.92
1.7	1×10^{-3} + 0.01 g of solid	1.6
3.0	1×10^{-3} + 0.01 g of solid	1.3
6.0	1×10^{-3} + 0.01 g of solid	1.0
3.5	3×10^{-3}	1.1
6.2	3×10^{-3}	0.33
11.3	1×10^{-3} + 0.01 g of solid	1.0
13.1	1×10^{-3}	0.15
None	1×10^{-3} + 0.01 g of solid	$\leqq 0.001$

Weak light emission is also observed from singlet oxygen and BPEA or DPA in the absence of ketene. The emission spectrum agrees well with the fluorescence of the BPEA used and the quantum yield is low, $\sim 1 \times 10^{-7}$ einstein mol^{-1} of $^1O_2$. An energy pooling

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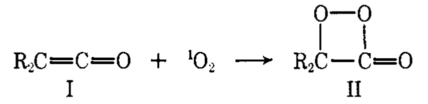
[1] R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **90**, 537 (1968); **91**, 5358 (1969).

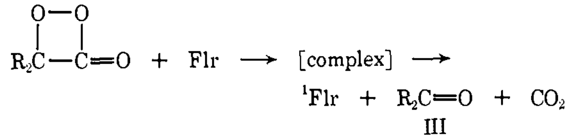
and energy transfer process from $^1O_2$ must be involved in this emission.[2]

The diphenylketene reaction produced benzophenone (40%) and carbon dioxide along with diphenylacetic acid (60%), a hydrolysis product. The products of the diphenylketene glycol acetal reaction were benzophenone, ethylene carbonate, and 2-hydroxyethyl diphenylacetate, a hydrolysis product. All these compounds were identified by the comparison of their ir spectra with those of authentic samples.

Dioxetane decomposition is now accepted as the key step in a number of chemiluminescent reactions.[3] Moreover, the reaction of singlet oxygen and activated olefins produces dioxetanes which decompose to carbonyl cleavage products.[3c,4] Thus, the chemiluminescent light emission and the carbonyl products suggest that the ketene–singlet oxygen reaction proceeds through dioxetanone II and that the chemiluminescence observed is derived from the decomposition of II as shown below, where R = H or phenyl.



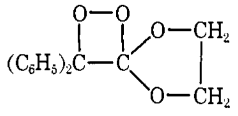
(1)



(2)

$$^1\mathrm{Flr} \longrightarrow h\nu + \mathrm{Flr} \qquad (3)$$

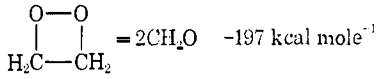
The probable product of the diphenylketene glycol acetal reaction is a dioxetane (IV) which produces sub-



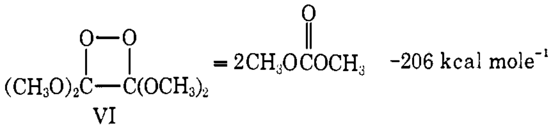
IV

stantially weaker light emission than available from diphenyldioxetanone or from dioxetanedione.[5] Thus, the structure of the dioxetane has an important bearing on the light emission. This structural dependence should be considered in terms of the general requirements for high chemiluminescence efficiency. These requirements include:[3b,5] (a) sufficient energy of decomposition, ~75 kcal mol^{-1}, to excite the fluorescer, (b) an inherent tendency to form decomposition products in their singlet excited state, and (c) complex formation or at least collisional contact between dioxetane and fluorescer at the time of decomposition.

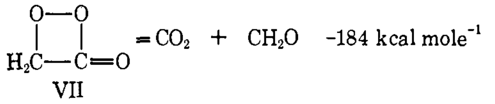
The decomposition energies of four dioxetane derivatives and some of their dimers were calculated by the EHMO method[6] as



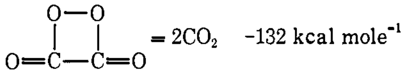
V (4)



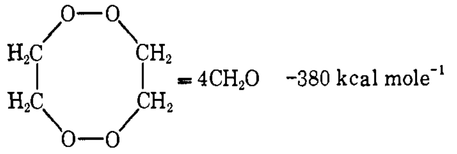
VI (5)



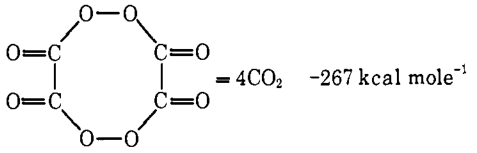
VII (6)



VIII (7)



IX (8)



X (9)

Although the MO method used is admittedly approximate in nature, the results clearly indicate that all six reactions could release ample energy to excite the fluorescers under discussion. More quantitative statements must be considered with caution because of the uncertainties in the molecular geometries of the intermediates. However, the following results are of interest. The sp^2 carbons in VII and VIII appear to lower the decomposition energy and thereby could increase the stability and the lifetime of the dioxetane molecule. The four methoxy groups in VI do not seem to change the decomposition energy strongly. There appears to be some driving force toward the dimerization of V, approximately 7 kcal mol^{-1}. In contrast to V the dimerization of VIII is not energetically favored. The Woodward–Hoffman rule predicts that the concerted decomposition of all four dioxetanes considered here should lead to excited products.[7]

We conclude from our experimental results and calculations that dioxetane intermediates containing at least one sp^2 carbon may be substantially more capable, in

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(2) (a) S. J. Arnold, N. Finlayson, and E. A. Ogryzlo, *J. Chem. Phys.*, **44**, 2529 (1966); E. A. Ogryzlo and A. E. Pearson, *J. Phys. Chem.*, **72**, 2913 (1968); T. Wilson, *J. Amer. Chem. Soc.*, **91**, 2387 (1969); (b) the singlet energies of the fluorescers BPEA (E_s = 58.2 kcal mol^{-1})[2c] and DPA (E_s = 70.8 kcal mol^{-1})[2d] are substantially higher than those of violanthrone and rubrene used by Ogryzlo, *et al.*, and Wilson, respectively; (c) L. J. Bollyky, B. G. Roberts, R. H. Whitman, and J. E. Lancaster, *J. Org. Chem.*, **34**, 836 (1969); (d) measured by B. G. Roberts in dimethyl phthalate solution by the method of H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(3) (a) F. McCapra and D. G. Richardson, *Tetrahedron Lett.*, 3167 (1964); F. McCapra, *Chem. Commun.*, 155 (1968); (b) M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969), and references therein; (c) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); (d) F. McCapra and R. A. Hamm, *Chem. Commun.*, 442 (1969); (e) E. H. White and M. J. C. Harding, *J. Amer. Chem. Soc.*, **86**, 5686 (1964); F. McCapra and Y. C. Chang, *Chem. Commun.*, 522 (1966); T. A. Hopkins, H. H. Seliger, E. H. White, and M. W. Cass, *J. Amer. Chem. Soc.*, **89**, 7148 (1967); F. McCapra, Y. C. Chang, and V. P. Francois, *Chem. Commun.*, 22 (1968).

(4) W. Fenical, D. R. Kearns, and F. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969); D. R. Kearns, *ibid.*, **91**, 6554 (1969); ref 3d.

(5) (a) L. J. Bollyky, M. Loy, B. G. Roberts, R. H. Whitman, A. V. Iannotta, A. M. Semsel, and M. M. Rauhut, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract O-169; M. M. Rauhut, L. J. Bollyky, B. G. Roberts, M. Loy, R. H. Whitman, A. V. Iannotta, A. M. Semsel, and R. A. Clarke, *J. Amer. Chem. Soc.*, **89**, 6515 (1967); (b) H. F. Cordes, H. P. Richter, and C. A. Heller, *ibid.*, **91**, 7209 (1969).

(6) Calculations by Dr. M. K. Orloff using the method of R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(7) R. Hoffmann and R. D. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

general, of chemiluminescence excitation than those containing no sp^2 carbon. However, our results are insufficient to determine the cause of the only weak light emission from dioxetanes such as IV that contain no sp^2 carbon. The possible explanations include: (a) the dimerization of IV to form a cyclic peroxide analogous to IX, (b) that IV forms no complex prior to decomposition and the singlet excited products undergo intersystem crossing preferentially to energy transfer, or (c) a nonconcerted decomposition of IV. All three would lead to a short lifetime of the highly energetic dioxetane molecule. Further experimental work is required to elucidate these points.

Acknowledgment. The author thanks Dr. M. M. Rauhut for the helpful discussions, Mr. B. G. Roberts for some of the spectrofluoroscopic measurements, and Mr. N. B. Colthup for the infrared measurements. Special thanks are due to Dr. M. K. Orloff for carrying out the EHMO calculations.

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A New and Convenient Method for the Reduction of an Aromatic Carboxyl to a Methyl Group

Sir:

A reasonable number of methods are available for the reduction of carboxylic acids to either alcohols[1-5] or aldehydes.[6,7] However, there exists no simple procedure whereby complete reduction of the carboxyl moiety to a methyl group can be effected.[8]

We are hereby reporting such a procedure which appears to be general for many aromatic acids. The overall transformation can be depicted by eq 1. The

$$\mathrm{ArCO_2H} \xrightarrow[\mathrm{CH_3CN;\ \Delta}]{\mathrm{SiHCl_3}} \xrightarrow[\Delta]{\mathrm{R_3N}} \xrightarrow[\mathrm{aq\ MeOH;\ \Delta}]{\mathrm{KOH}} \mathrm{ArCH_3} \qquad (1)$$

yield of reduction product for a representative series of aromatic acids is quite good (Table I).

While the sequence shown in eq 1 involves essentially three steps, all of these can be carried out sequentially without any purification of intermediates.

In a typical experiment, 0.6 mol of trichlorosilane and 0.1 mol of 3,5-dimethylbenzoic acid in 80 ml of acetonitrile were refluxed 1 hr. After cooling, 0.264 mol of tri-*n*-propylamine was added so that the temperature did not rise above 15°. After the mixture was refluxed for 16 hr it was diluted to 850 ml with diethyl ether and filtered to remove the amine hydrochloride. The distillate was concentrated to remove the ether and acetonitrile, whereupon 50 ml of methanol was added to the nonvolatile oily residue and the solution refluxed for 1 hr. One mole of potassium hydroxide dissolved in a solution of 95 ml of methanol and 25 ml of water was then added slowly, and the resulting suspension refluxed for 19 hr. It was then diluted with 600 ml of water and extracted with pentane. The latter was washed with 50 ml of 2 *N* hydrochloric acid. Removal of the solvent and distillation gave 0.082 mol (82%) of mesitylene.

Table I. Reduction of Aromatic Acids to Substituted Benzenes[a,b]

Starting acid	Product[c,d]
Benzoic	Toluene (78)
m-Toluic	*m*-Xylene (82)
p-Toluic	*p*-Xylene (74)
3,5-Dimethylbenzoic	Mesitylene (82)
p-Chlorobenzoic	*p*-Chlorotoluene (94)
p-Bromobenzoic	*p*-Bromotoluene (94)
Phthalic	*o*-Xylene (64)

[a] In every case, the same reaction conditions as those outlined in the text for entry 4 were employed, except that only 0.05 mol of phthalic acid was used. [b] In each case, approximately 0.2 mol of amine hydrochloride was isolated. [c] Products were identified by matching ir spectra with those of authentic samples. [d] The values in parentheses are the percentage yield of isolated product, based upon the weight of starting acid.

While exact mechanistic details of the reduction must remain speculative at this time, certain observations have been made which are suggestive of the overall pathway. If one uses benzoic acid as the substrate and interrupts the reaction after the first step (refluxing with trichlorosilane in acetonitrile), an excellent yield of benzoic anhydride (74%) can be realized after distilling the residue.[9] It was noted, also, that benzoic anhydride like benzoic acid[10] undergoes reductive silylation in the presence of trichlorosilane and tri-*n*-propylamine, forming benzyltrichlorosilane (eq 2).

$$\mathrm{(C_6H_5CO)_2O} \xrightarrow[\mathrm{R_3N;\ \Delta}]{\mathrm{SiHCl_3}} \mathrm{C_6H_5CH_2SiCl_3} \qquad (2)$$

It is well established that silanes, like benzyltrichlorosilane, are cleaved by aqueous base,[11] forming toluene as one of the products in this case. If one can generalize from benzoic acid to all the examples in Table I, the overall reduction process can be depicted by eq 3.

$$\mathrm{ArCO_2H} \xrightarrow[\Delta]{\mathrm{SiHCl_3}} \begin{array}{c}\mathrm{(ArCO)_2O}\\ \mathrm{or}\\ \mathrm{(ArCO_2)_{\mathit{x}}SiHCl_{\mathit{y}}}\end{array} \xrightarrow[\mathrm{R_3N;\Delta}]{\mathrm{SiHCl_3}}$$
$$\mathrm{ArCH_2SiCl_3} \xrightarrow[\Delta]{\mathrm{KOH;\ MeOH}} \mathrm{ArCH_3} \qquad (3)$$

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(1) V. Bazant, *et al.*, *Tetrahedron Lett.*, 3303 (1968).

(2) H. S. Broadbent, G. C. Campbell, W. J. Bartley, and J. H. Johnson, *J. Org. Chem.*, **24**, 1847 (1959).

(3) H. C. Brown and B. C. Subba Rao, *ibid.*, **22**, 1135 (1957).

(4) H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **77**, 3164 (1955).

(5) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947).

(6) S. Ono and T. Yamauchi, *Bull. Chem. Soc., Jap.*, **25**, 404 (1952).

(7) H. A. Staab and H. Braunling, *Justus Liebigs Ann. Chem.*, **654**, 119 (1962).

(8) (a) Such a transformation can be achieved by reduction of the acid to the alcohol with lithium aluminum hydride and conversion of the alcohol to the tosylate, followed by a second reduction either with lithium aluminum hydride or Raney nickel and hydrogen. See N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience, New York, N. Y., 1956, p 855. Benzylic-type alcohols can also be reduced directly with hydrogen under pressure in the presence of various catalysts. See, for example, R. L. Shriner and R. Adams, *J. Amer. Chem. Soc.*, **46**, 1683 (1924). (b) Benzoic acid can be reduced to toluene with rhenium-type catalysts and hydrogen at high temperatures and pressures. See ref 2 and H. S. Broadbent and D. W. Seegmiller, *J. Org. Chem.*, **28**, 2347 (1963).

(9) It is quite possible that such anhydrides are formed thermally *during* this distillation from the aryloxy- or acyloxysilanes (in the case of aliphatic acids) which are present. Further work will be needed to ascertain whether benzyltrichlorosilane is being formed from benzoic anhydride or the benzoyloxysilanes.

(10) R. A. Benkeser and J. M. Gaul, *J. Amer. Chem. Soc.*, **92**, 720 (1970).

(11) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp 143–146.