

to the comparable alkyl complexes. House and Umen have suggested that a species of this type is responsible for the observed reduction of isophorone during conjugate addition.⁶

The experiments summarized in Table I indicate that the preferred reducing agent for unsaturated carbonyl derivatives is the 1-pentynyl complex (1). The ability to function as a reducing agent appears qualitatively to decrease in the order of nontransferable ligand: 1-pentyne > SPh > *O-t*-Bu, with the latter two being significantly less effective (apparently less reactive). We have also found that added hexamethylphosphoramide (HMPA) appears to facilitate somewhat the reduction in cases where the β -carbon is highly substituted. The HMPA probably functions in one of two ways: (1) by mediating electron transfer or (2) by increasing the nucleophilicity of the complex. The reductions are regiospecifically 1,4 and other normally reducible functionalities are unaffected.

The results of the reduction of a series α,β -unsaturated carbonyl compounds utilizing the most effective complex (1) may be found in Table II. Acyclic and more acidic cyclic carbonyl compounds generally give somewhat lowered yields and require low temperature conditions. This apparently is due to the relatively basic nature of these reducing agents which promotes proton transfer and polymerization. However, to the extent that reduction occurs, it occurs specifically in the 1,4 sense.

The stereochemistry of reduction is generally the expected antiparallel entry of hydride.⁷ In the case of 4 the results are comparable to hydrogenation.⁸ As the substitution surrounding the β -carbon increases, the reduction becomes more sluggish and is somewhat less selective. The reduction of octalone 5 produces a *cis*:*trans* ratio of 70:30 which is somewhat less specific than hydrogenation (80:20).⁹

Particularly noteworthy among the examples cited in Table II is the reduction of doubly unsaturated 6. The regiospecific reduction realized would not be trivially attainable by catalytic reduction. Initial attempts to utilize the complexes 1-3 for partial reduction of α,β -acetylenic derivatives have not been successful.

A typical experimental procedure follows. $\text{Cu}^{\text{I}}\text{H}$ is prepared from Cu^{I} (purified)-pyridine complex and diisobutylaluminum hydride in toluene ($\sim 2 M$) at *ca.* -50° under nitrogen.¹ The $\text{Cu}^{\text{I}}\text{H}$ is precipitated as a brown solid by dilution with dry ether, and washed four-six times with ether to remove residual aluminum salts and pyridine. A solution of lithio-1-pentyne (6 mmol) 0.5-1.0 *M* in dry tetrahydrofuran (THF)¹⁰ is added to the $\text{Cu}^{\text{I}}\text{H}$ (6 mmol) and the mixture shaken at -50° , affording an almost clear dark brown solution. This solution is diluted with THF ($\sim 0.25 M$) and HMPA (10% by volume) is added if desired. The unsaturated carbonyl compound (1 mmol) in a small amount of THF is added and the mixture is stored at the

desired temperature for the designated time period. After quenching with 10% NH_4Cl solution, the precipitated solids are removed by filtration and the products isolated by extraction (ether). Purification by distillation or chromatography then affords the reduction products.

We are presently exploring conditions for the successful reduction of other classes of substrates including those of the acetylenic type, and the chemistry of the derived enolate species. The present report demonstrates that (1) hydride is successfully transferred by copper "ate" complexes in the presence of a second nontransferable ligand, (2) the regiospecificity and functional selectivity of these reagents is high, and (3) the stereoselectivity is comparable to that obtained by hydrogenation in most cases. The selective nature of these complexes complements existing methods for this transformation and should make them useful reducing agents for multifunctional molecules.

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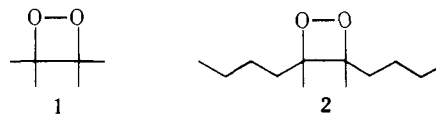
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Thermal and Photochemical Decomposition of 3,4-Dimethyl-3,4-di-*n*-butyl-1,2-dioxetane. Competitive Generation of Singlet and Triplet 2-Hexanone¹

Sir:

Numerous reports have appeared recently describing the thermal decomposition of various 1,2-dioxetanes to give electronically excited carbonyl products, as evidenced by chemiluminescence, sensitization, photochemical products, etc.² In the majority of cases the apparent total yield of excited species from simple alkyl-1,2-dioxetanes has been on the order of 10% or lower.^{2a-d} However, in a recent communication, Turro and coworkers reported that tetramethyl-1,2-dioxetane (1) yields triplet acetone (50%) with only a minor population of singlet (<1%) as primary thermolysis products.^{2f}

In light of the provocative theoretical implications of such a high triplet yield, we have investigated the closely related 3,4-dimethyl-3,4-di-*n*-butyl-1,2-dioxetane (2).



We report here results which differ surprisingly from those of Turro, *et al.*

(1) Supported by National Science Foundation Grant No. GP 25,790.

(2) (a) W. H. Richardson, F. C. Montgomery, and M. B. Yelvington, *J. Amer. Chem. Soc.*, **94**, 9277 (1972); (b) H. Güsten and E. F. Ullman, *ibid.*, **92**, 6074 (1970); (c) E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, **92**, 2167 (1970); (d) P. D. Wildes and H. White, *ibid.*, **93**, 6286 (1971); (e) T. Wilson and A. P. Schaap, *ibid.*, **93**, 4126 (1971); (f) N. J. Turro and P. Lechtken, *ibid.*, **94**, 2886 (1972); (g) W. Adam and J. C. Liu, *ibid.*, **94**, 2894 (1972), and additional references are contained therein.

(6) H. O. House and M. Umen, *J. Org. Chem.*, **38**, 3893 (1973).

(7) (a) J. A. Marshall and N. H. Andersen, *J. Org. Chem.*, **31**, 667 (1966); (b) J. Valls and E. Toromanoff, *Bull. Soc. Chim. Fr.*, 758 (1961).

(8) Authentic mixture prepared by hydrogenation (1 atm) over palladium on charcoal in ethanol ($\sim 95:5$; *cis*:*trans*) reported 100% *cis* R. L. Augustine and A. D. Broom, *J. Org. Chem.*, **25**, 802 (1960).

(9) R. Futaki, *J. Org. Chem.*, **23**, 251 (1958); ratio determined by nmr.

(10) Prepared at 0° in dry tetrahydrofuran (THF) from 1-pentyne and *n*-butyllithium (1:1 molar ratio).

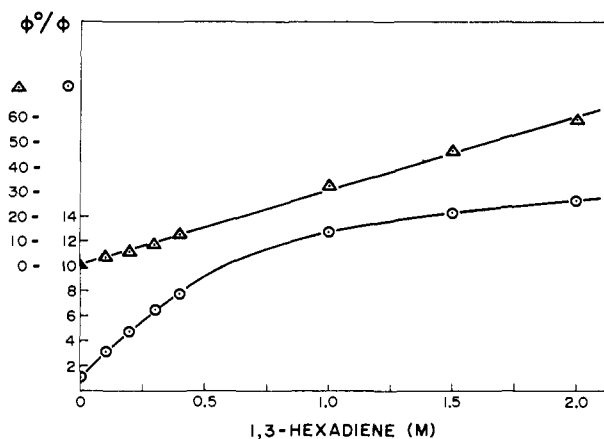
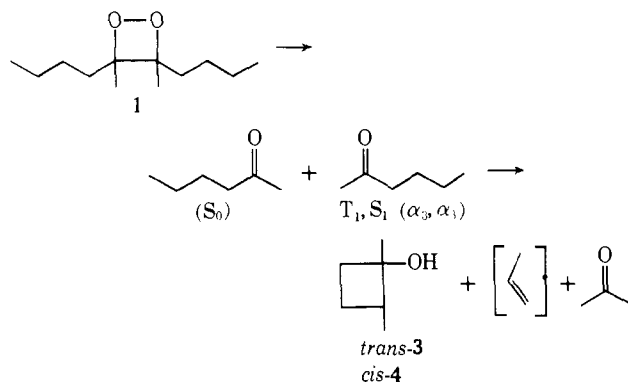


Figure 1. Quenching of cyclobutanol production from 0.05 *M* 2 in decalin at 50° with 1,3-hexadiene: total cyclobutanol yield, ○; cyclobutanol yield minus the unquenchable (singlet) component, △.

Heating 2 for 24 hr in 0.01–0.05 *M* decalin solution at 50° results in quantitative conversion to 2-hexanone and chemelectronic products (Scheme I).³ The average

Scheme I



yields of the chemelectronic products, acetone and cyclobutanols 3 and 4, are 3.0, 0.67, and 0.47%, respectively.⁴ The rate of thermolysis of 2 in decalin is similar to that of 1 in nonpolar solvents;⁵ the reaction is first order between 50 and 80°, with $\Delta H^\ddagger = 24.8 \pm 0.3$ kcal and $\Delta S^\ddagger = -3.6 \pm 1.0$ cal/deg.

The products of 2-hexanone type II photochemistry provide a unique counting technique for both the excitation yield and multiplicity of initially generated carbonyl fragments, since the photochemistry of this type is well understood.⁶ We have carefully reinvestigated the photochemical behavior of 2-hexanone under conditions comparable to those used in the thermal decomposition of 2. The results are summarized in Scheme II.⁷ Each number shown represents the frac-

(3) A 1:1 mixture of the cis and trans isomers of 2 was prepared by the procedure of K. R. Kopecy and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969). Both isomers decomposed at an identical rate. A chain decomposition of dioxetane (degassed or aereated) was not observed at the concentrations used, probably because of the short lifetime of triplet 2-hexanone.

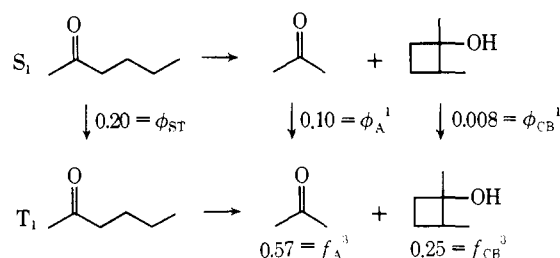
(4) The same cyclobutanol isomer ratio was obtained by photolysis of 2-hexanone in decalin at 50°.

(5) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **95**, 264 (1973).

(6) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, **5**, 92 (1972); see also P. J. Wagner, *ibid.*, **4**, 168 (1971).

(7) See N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, **91**, 7551 (1969) and N. C. Yang and D. R. Coulson, *ibid.*, **88**, 4511 (1966) for a comparison with 2-hexanone photochemistry at 25°.

Scheme II



tion of excited molecules (S_1 or T_1) which reacts to form a given product.

If photoexcited and chemically excited states of 2-hexanone behave identically, then direct formation of 2-hexanone triplet in the thermolysis of 2 would produce acetone and cyclobutanol efficiently and in the ratio 2.3:1. Formation of singlet 2-hexanone would give a lower yield of photoproducts but a higher relative yield of acetone, characteristic of direct irradiation (3.7:1). For each decomposition run, the acetone-cyclobutanol ratio fell between these values, with an average of 2.65 ± 0.1 . Equations 1 and 2 relate the observed thermal yields of acetone and cyclobutanols (ϕ_A^{diox} and ϕ_{CB}^{diox}) to the actual singlet and triplet excitation yields (α_1 and α_3) in terms of the parameters measured in the photochemical system. The values f_A^3 and f_{CB}^3 denote the efficiencies of product formation from the triplet of 2-hexanone. Solution of simultaneous equations 1 and 2 yields $\alpha_1 = 5\%$ and $\alpha_3 = 3.5\%$.

$$\phi_A^{\text{diox}} = \alpha_1(\phi_A^1 + \phi_{ST}f_A^3) + \alpha_3(f_A^3) \quad (1)$$

$$\phi_{CB}^{\text{diox}} = \alpha_1(\phi_{CB}^1 + \phi_{ST}f_{CB}^3) + \alpha_3(f_{CB}^3) \quad (2)$$

Both the overall low yield of excited species and the high relative value for the singlet were unexpected in light of the earlier work on dioxetane 1.^{2e} As confirmation of our findings, a Stern-Volmer plot of 1,3-hexadiene quenching of cyclobutanol formation was obtained for the thermolysis (Figure 1). The triplet quenching slope is $30 M^{-1}$,⁸ and the yields of cyclobutanol derived from singlet and triplet pathways are 0.056 and 1.08%, respectively. The thermal excitation yields in this case were obtained from eq 3 and 4, where $\phi_{CB_1}^{\text{diox}}$ and $\phi_{CB_3}^{\text{diox}}$ are the singlet (unquenchable) and triplet contributions to cyclobutanol formation as determined from the quenching plot; $\alpha_1 = 7\%$ and $\alpha_3 = 3\%$. This experiment represents an independent confirmation of the excitation values obtained above.

$$\phi_{CB_1}^{\text{diox}} = \alpha_1\phi_{CB}^1 \quad (3)$$

$$\phi_{CB_3}^{\text{diox}} = \alpha_1\phi_{ST}f_{CB}^3 + \alpha_3f_{CB}^3 \quad (4)$$

Irradiation of 2 (at 25° in 0.03 *M* decalin solution) with light >360 nm (Optical Ind., Inc., filter No. O3-FCG129) efficiently yields 2-hexanone and small amounts of acetone (2.3%) and cyclobutanol (0.86%). The excitation yields were derived by the same method used for the thermolysis (using photochemical data for 2-hexanone at 25°); $\alpha_1 = 4\%$ and $\alpha_3 = 2.2\%$. The

The efficiency of product formation from the triplet state is not affected by higher temperature. That the intersystem crossing yield is diminished and the quantum yield of singlet products is increased slightly probably stems from an enhanced rate of singlet interaction with the γ -hydrogen at 50°.

(8) The triplet quenching slope is $32 M^{-1}$ for 1,3-hexadiene quenching in decalin at 50° for the photolysis of 2-hexanone.

corresponding yields reported for **1** at 366 nm are 10 and 43%.⁹

In summary, the efficient spin inversion during photochemical and thermochemical decomposition of **1** is not found with **2**. Initial formation of ground-state 2-hexanone from **2** accounts for nearly all (>90%) of the products derived thermally or photochemically; thus **2** resembles most of the previous dioxetanes in its low excitation yield.

Kearns has offered a possible explanation of how chemical excitation might occur in 1,2-dioxetane systems.¹⁰ A crossing between the ground-state energy surface of the dioxetane and an upper level surface, which correlates with an excited state of the product, was proposed as a possible concerted pathway. Turro has pointed out that the orbital symmetry change corresponding to a shift from an all- σ to an n, π^* system could give strong spin-orbital coupling leading to enhanced spin inversion.⁵ However, Richardson has suggested that diradical states are intermediate, because of compelling energy considerations.¹¹

We believe that the contrasting behavior of **1** and **2** represents either (a) differences in partitioning of an intermediate species such as a diradical or (b) differences in efficiency of vibronic coupling between nonintersecting segments of ground- and excited-state energy surfaces. We are not able to account for these differences at the present time. It is particularly important that the *photochemical* and *thermochemical* triplet excitation yields *do not differ* significantly within each system.^{12,13} Unique behavior in this system on photosensitized decomposition will be reported shortly.

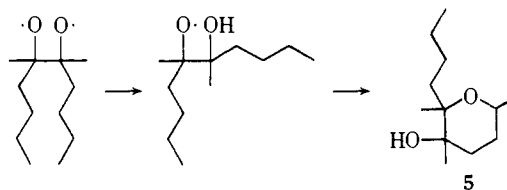
(9) N. J. Turro, P. Lechtken, A. Lyons, R. R. Hautala, E. Carnahan, and T. J. Katz, *J. Amer. Chem. Soc.*, **95**, 2035 (1973).

(10) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971).

(11) H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, **92**, 6553 (1970); W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *ibid.*, **94**, 1619 (1972).

(12) This observation suggests that in the case of a spin-forbidden concerted process, similar spin-orbital factors must couple both the ground and first excited state surfaces of the dioxetane with those of the n, π^* triplet ketone.

(13) A referee has questioned whether some of the products might not derive from γ -hydrogen abstraction in a diradical intermediate. In our consideration of this possibility, we felt that **5** should accompany any such process, and no evidence for **5** was found.



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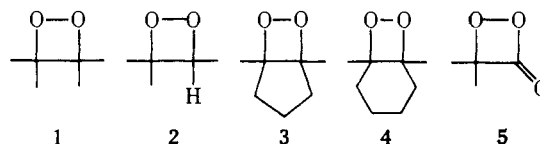
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Indirect Chemiluminescence by 1,2-Dioxetanes. Evaluation of Triplet-Singlet Excitation Efficiencies. A Long Range Singlet-Singlet Energy Transfer and an Efficient Triplet-Singlet Energy Transfer

Sir:

A great deal of recent research in chemiluminescence has been focused on the mechanism of conversion of chemical energy into electronic energy¹ and in the

utilization² of the thermally generated electronically excited states for "photochemistry in the dark." Indirect chemiluminescence (*i.e.*, emission from an additive rather than a primary chemiexcited product) has been employed to both amplify the intensity of emission and to study the mechanism of energy transfer processes. For example, Belakov and Vasilev³ have extensively studied the use of anthracenes as energy acceptors for triplet ketones and Wilson and Schaap⁴ have used anthracenes as energy acceptors in their study of the thermolysis of *cis*-diethoxy-1,2-dioxetane. These earlier reports^{3,4} assumed that the indirect chemiluminescence of anthracene (identified as anthracene fluorescence) was due exclusively to triplet (carbonyl) to singlet (anthracene) energy transfer and that the rate constant for this spin-forbidden process is, at best, about 100 times less than that for the spin-allowed alternative, triplet (carbonyl) to triplet (anthracene) energy transfer. We provide evidence that indirect chemiluminescence by singlet-singlet energy transfer is dominant in the case of "nonheavy atom" substituted anthracenes (*e.g.*, 9,10-diphenylanthracenes, DPA) and that triplet-singlet energy transfer is the dominant mechanism in the case of "heavy atom" substituted anthracenes (*e.g.*, 9,10-dibromoanthracene, DBA). We then use our observations to (a) evaluate the triplet-singlet excitation efficiencies of several 1,2-dioxetanes (**1-5**) and (b) evaluate



the rate constants for singlet-singlet and triplet-singlet energy transfer and compare these to values for triplet-triplet energy transfer.

The key experiments of this study involve the measurements of the indirect chemiluminescence (fluorescence) of DPA and DBA, chemiexcited by thermolysis of the 1,2-dioxetanes **1**, **2**, **3**, **4**, and **5**. In all cases, the change in concentration of dioxetane is small (<0.1%) during the period of measurement. The intensity of indirect chemiluminescence, I_{CL} , is given in eq 1, where

$$I_{CL} = R[(\phi_*^S \phi_{ET}^{SS} \phi_{FA}^A) + (\phi_*^T \phi_{ET}^{TS} \phi_{FA}^A)] \quad (1)$$

R is the rate of disappearance of dioxetane, ϕ_*^S (ϕ_*^T), ϕ_{ET}^{SS} (ϕ_{ET}^{TS}), and ϕ_{FA}^A are the efficiencies of singlet (or triplet) formation from the dioxetane, singlet-singlet (or triplet-singlet) energy transfer from excited donor to anthracene, and anthracene fluorescence, respectively. Experimentally, it is found that specific triplet ketone quenchers (1,3-dienes, oxygen, acrylonitrile) *dramatically decrease the indirect chemiluminescence of DBA, but have a negligible effect on the indirect chemiluminescence of DPA*. From this striking result we conclude that the dominant mechanism for indirect chemiluminescence of DBA is triplet-singlet energy transfer whereas the dominant mechanism for indirect chemilumines-

(1) N. J. Turro and P. Lechtken, *Pure Appl. Chem.*, **33**, 363 (1973); *J. Amer. Chem. Soc.*, **95**, 264 (1973), and references therein.

(2) E. White, J. Wiecko, and C. C. Wei, *J. Amer. Chem. Soc.*, **92**, 2167 (1970); E. White, J. Wiecko, and D. F. Roswell, *ibid.*, **91**, 5194 (1969); H. Gisten and E. F. Ullman, *Chem. Commun.*, 28 (1970).

(3) V. A. Belakov and R. F. Vasilev, *Photochem. Photobiol.*, **11**, 179 (1970).

(4) T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971).