

Photochemical Instrumentation. All photolyses were carried out by using a 1200 W medium-pressure Hanovia lamp in a water-cooled immersion well. A 1-cm pathlength filter solution consisting of 27.0 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 30.0 g of NaNO_2 , and 50 mL of concentrated NH_4OH diluted with water to 1000 mL was used. This filter isolates the Hg lines at 405 and 436 nm (ref 32, p 737).

Irradiation Procedures. All solutions for analytical photolyses were placed in matched Bausch and Lomb Spectronic 20 test tubes (capacity ~5 mL). Concentrations of substrates were $(1-2) \times 10^{-2}$ M and of DCA or CNA, 10^{-4} M. The tubes were stoppered with serum caps, and O_2 or N_2 was bubbled through the solutions for 3 min prior to irradiation. During photolysis, the tubes rotated around the light source on a merry-go-round. After irradiation, an appropriate substrate was added for internal standardization in the GLPC analysis, carried out on a Hewlett-Packard Model 5720A gas chromatograph using a 50 cm \times $1/8$ in. stainless-steel column packed with 10% UC-W 98 on 80-100 mesh WAW-DMCS or a 120 cm \times $1/8$ in. stainless-steel column packed with 10% Carbowax 20M on 80 \times 100 mesh Chromosorb W. For all quantitative determinations, the GLPC analyses were carried out in triplicate. In these experiments, the conversion of substrate was always kept below 10%. Irradiation times leading to >90% conversion were 30 min for **1**, 60 min for **12** and **14**, and 180 min for **18** under these conditions.

In preparative photolyses, tubes of 100- or 500-mL capacity were used. Oxygen was constantly bubbled through the solution during irradiation.

Photolysates were concentrated on a rotary evaporator and the residues chromatographed (Silica Gel, 2.5 \times 40 cm) and eluted with 0-30% benzene in hexane. Eluted fractions were analyzed by GLPC.

Quantum Yields. Potassium ferrioxalate and the procedure described by Calvert and Pitts were used.³² The light source was a 200-W Hg-Xe lamp, and the 405-nm line was isolated by a Jarrell-Ash monochromator. The light intensity was determined twice before and once after the actual photolysis. No change in light intensity was detected during these experiments. The photolysis of **1** and DCA were carried out to ~10% conversion of **1**. The photolysate was analyzed by GLPC using an internal standard and determination of GLPC response factors. The quantum yields were determined three times. The photooxygenation of **1** was used as an actinometer for the measurements of the quantum yields for the photooxygenation of **12**, **14**, and **18**, which were irradiated on the merry-go-round.

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Photoaddition of Biacetyl and Alkenes. Reaction Stereochemistry, Multiplicity, and Photokinetics

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Abstract: Quantum yields are reported for the photoaddition of biacetyl with the alkenes indene, 2,3-dimethyl-2-butene, furan, and 1,2-dimethoxyethene in benzene solution. The dependence of quantum efficiencies on alkene concentration is consistent with a photoaddition mechanism involving biacetyl triplets. The quenching of fluid solution biacetyl phosphorescence has been observed, and quenching constants correlate with the electron-donor ability (ionization potentials) of the alkenes. Photoaddition of biacetyl and 1,2-dimethoxyethene is nonstereospecific, and oxetane formation is accompanied by the isomerization of the starting alkene. Stereochemical results are used to estimate relative rates of cleavage, closure, and stereorandomizing bond rotation in biradicals, proposed intermediates in photoaddition. Exciplexes of triplet biacetyl and alkenes are proposed as primary photochemical intermediates (precursors to biradicals) on the basis of the stereochemical, emission quenching, and other data.

The solution photochemistry of biacetyl and related dicarbonyl compounds appears to be dominated by reactions involving hydrogen abstraction from solvent or another reagent followed by varied combination of the photogenerated radicals.¹ On the other hand, a number of recent reports^{2,3} have described photoaddition of biacetyl and unsaturated substrates under circumstances where hydrogen abstraction might have taken place but did not prevail. Thus, the conjugated dicarbonyl functionality appears to join the larger class of simple alkanones and alkanals which readily participate in the Paterno-Buchi (cycloaddition) and related reactions.⁴

The quantitative aspects of this comparison of dicarbonyls and other aldehydes and ketones are not well understood although the

mechanism of biacetyl addition is partially known. Several alkenes have been shown to quench the phosphorescence of biacetyl,^{2a,d,e} but in a number of cases biacetyl fluorescence emission can also be quenched.⁵ These results in general permit that either singlet or triplet states of biacetyl may be reactive. Emission quenching and quantum yield results indicate that a triplet path is dominant for biacetyl/1,2-diethoxyethene photoaddition.^{2c} Labeling studies^{2a} further show that 1,4 biradicals may be important intermediates which follow the initial interaction of biacetyl and quenchers and lead to oxetane and "ene-type" addition products.

In the spirit of earlier mechanistic analyses^{4,6} of alkanone and alkanal addition, we have examined in detail the interaction of excited biacetyl with a variety of unsaturated compounds. Luminescence results and the profile of quantum yield of photoaddition as a function of the concentration of addends allow the assignment of the reactive excited state. A stereochemical test provides information on the nature of penultimate intermediates involved in photoaddition.

Cycloaddition reactions which employ visible absorbing chromophores as sensitizers or substrates are currently of interest as

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(2) (a) H.-S. Ryang, K. Shima, and H. Sakurai, *J. Am. Chem. Soc.*, **93**, 5270 (1971); (b) H.-S. Ryang, K. Shima, and H. Sakurai, *J. Org. Chem.*, **38**, 2860 (1973); (c) H.-S. Ryang, K. Shima, and H. Sakurai, *Tetrahedron Lett.*, 1041 (1970); (d) R. R. Sauer, P. C. Valentini, and E. Tavss, *ibid.*, 3129 (1975); (e) T.-J. Lee, Ph.D. Dissertation, Columbia University, 1972.

(3) Photoaddition of biacetyl and other dicarbonyls to alkynes has also been reported: A. Mosterd, H. J. Matser, and H. J. T. Bos, *Tetrahedron Lett.*, 4179 (1974).

(4) (a) N. C. Yang, M. H. Hui, D. M. Shold, N. J. Turro, R. R. Hautala, K. Dawes, and J. C. Dalton, *J. Am. Chem. Soc.*, **99**, 3023 (1977); (b) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Acc. Chem. Res.*, **5**, 92 (1972); (c) D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968).

(5) B. M. Monroe, C.-G. Lee, and N. J. Turro, *Mol. Photochem.*, **6**, 271 (1974).

(6) (a) J. A. Barltrop and H. A. J. Carless, *J. Am. Chem. Soc.*, **94**, 8761 (1972); (b) K. Shima, T. Kubota, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **49**, 2567 (1976); (c) C. W. Funke and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 1902 (1976).

Table I. Stern–Volmer Constants for Quenching of Biacetyl Phosphorescence by Unsaturated Compounds^a

quencher	IP _v ^b , eV	k _q τ, M ⁻¹	τ, μs	10 ⁻⁶ k _q , M ⁻¹ s ⁻¹
2,5-dimethyl-2,4-hexadiene*	7.84 ^c	3.7 × 10 ⁵	214	1710
hexamethyl(Dewar benzene)*	7.90 ^d	1.0 × 10 ³	135	77
indole	7.92 ^e			210 ^f
N-methylpyrrole*	7.95 ^g	1.3 × 10 ³	169	74
trans-1-phenylpropene	8.28 ^h	4.8 × 10 ²	113	43
indene	8.33 ⁱ	1.2 × 10 ²	79	15
dihydropyran	8.34	9.1 × 10	68	13
cis-1,2-dimethoxyethene*	8.39 ^j	4.3 × 10 ⁴	225	233
tetramethylethylene	8.42 ^k	7.0 × 10	113	6.2
furan	8.89	3.1 × 10	113	2.8
norbornene	8.95			0.82 ^l
ethyl vinyl ether	9.07 ^j	2.6 × 10	79	3.3
cyclohexene	9.12 ^m			0.10 ⁿ
trans-2-hexene	9.16	4.6	68	0.68
methacrylonitrile	10.39	<0.5	79	<0.06

^a Degassed or nitrogen-purged (quenchers starred) benzene solutions. ^b Ionization potentials available except where noted: J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, L. K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bureau Stand.)* No. 26, (1969). ^c M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973). ^d G. N. Taylor, *Z. Phys. Chem. (Wiesbaden)*, **101**, 237 (1976). ^e L. N. Domelsmith, L. L. Munchausen, and K. N. Houk, *J. Am. Chem. Soc.*, **99**, 4311 (1977). ^f E. Fujimori, *Mol. Photochem.*, **6**, 91 (1974). ^g D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.*, **42**, 1064 (1970). ^h E. W. Fu and R. C. Dunbar, *J. Am. Chem. Soc.*, **100**, 2283 (1978). ⁱ P. E. Rakita, M. K. Hoffmann, M. N. Andrews, and M. M. Bursey, *J. Organomet. Chem.*, **49**, 213 (1973). ^j Reference 12. ^k W. Fuss and H. Bock, *J. Chem. Phys.*, **61**, 1613 (1974). ^l Reference 2d. ^m P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970). ⁿ H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

means for photochemical energy storage.⁷ The results for biacetyl allow comparison of more and less energetic chromophores, giving some understanding of what penalties in rate and quantum efficiency of reaction are to be paid in deploying relatively low-energy excited species.

Results

Luminescence Quenching. The room-temperature phosphorescence of nitrogen-purged or degassed solutions of biacetyl in benzene was quenched with varying efficiency on addition of unsaturated compounds. The quenchers employed are listed in Table I along with quenching data (k_qτ values) obtained from Stern–Volmer analysis. Biacetyl triplet lifetimes were calculated from the ratio of phosphorescence to fluorescence maxima by using as reference a recent measurement of the lifetime in benzene (τ = 135 μs, P/F ratio = 12)⁸ (see Experimental Section for details). With use of k_qτ values and adjusted lifetimes, quenching rate constants, k_q, were calculated as shown in Table I along with data from other laboratories.

The relationship between quenching rate and the structure of quenchers did not reveal an obvious dependence on either quencher triplet energies or hydrogen-donating properties. A reasonable fit of the data with the electron-donor properties of the alkenes and other quenchers was obtained as shown in the plot (Figure 1) of quenching constants and alkene ionization potentials (correlation coefficient = 0.903). Two quenchers appeared exceptional with quenching constants falling above the IP correlation line.

(7) (a) G. Jones, II, S.-H. Chiang, and P. T. Xuan, *J. Photochem.*, **10**, 1 (1979); (b) G. Jones, II, W. R. Bergmark, and T. Reinhardt, *Sol. Energy*, **20**, 241 (1978); (c) G. Jones, II, P. T. Xuan, and S.-H. Chiang in "Solar Energy: Chemical Conversion and Storage", R. B. King, C. R. Kutal, and R. R. Hautala, Eds., The Humana Press, Inc., Clifton, N.J., 1979.

(8) (a) N. J. Turro, K. Shima, G.-J. Chung, C. Tanielian, and S. Kanfer, *Tetrahedron Lett.*, submitted for publication. (b) N. J. Turro, private communication.

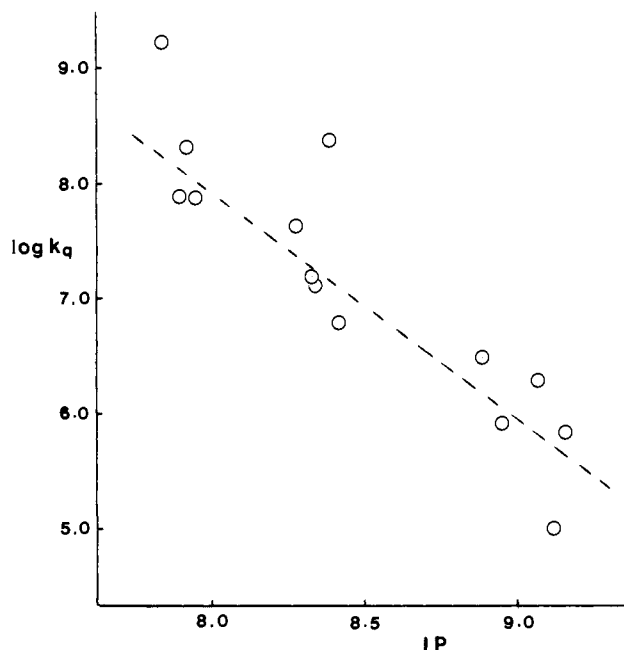


Figure 1. Rate constants for the quenching of biacetyl phosphorescence as a function of the vertical ionization potential (eV) of quenchers. See text for discussion of correlation line.

The higher rate for 2,5-dimethyl-2,4-hexadiene (DMH) is consistent with the imposition of an energy-transfer component to quenching, given the relatively low-lying triplet level for DMH ($E_T < 56$ kcal/mol⁹).

Such an artifact is less likely for *cis*-1,2-dimethoxyethene, since the isomerization of *cis*-DME induced by biacetyl triplets does not appear to involve energy transfer (vide infra). DME is in fact consistently a more effective quencher of ketone luminescence than expected, on the basis of the reported IP.¹² Rate constants are 5–10 times larger than predicted for acetone fluorescence quenching¹² and biacetyl fluorescence (vide infra) and phosphorescence quenching reported here.¹³ If DMH and DME are excluded from the IP dependence shown in Figure 1, a slope for the correlation line of -1.9 eV⁻¹ results, with $r = 0.944$.

Most of the unsaturated compounds were not efficient quenchers of biacetyl fluorescence in benzene ($k_q < 10^7$ M⁻¹ s⁻¹). Those with exceptionally good electron-donor properties (IP_v ≤ 8.0 eV) were moderate quenchers (DMH, $k_q = 3.4 \times 10^5$ M⁻¹ s⁻¹, and NMP, $k_q = 5.1 \times 10^8$ M⁻¹ s⁻¹, see below for DME), consistent with the results for biacetyl fluorescence quenching by alkenes in acetonitrile.⁵

Photoaddition to Furan, Indene, and Tetramethylethylene (TME). Preparative irradiation of biacetyl and furan or indene

(9) R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.*, **87**, 4230 (1965).

(10) Biacetyl triplet quenching by an energy-transfer mechanism has been reported.¹¹ Quenching by a mixed, energy- and charge-transfer, mechanism has been suggested.^{11d}

(11) (a) N. J. Turro and R. Engel, *J. Am. Chem. Soc.*, **91**, 7113 (1969); (b) A. W. Jackson and A. J. Yarwood, *Mol. Photochem.*, **8**, 255 (1977); (c) F. B. Wampler and R. C. Oldenborg, *Int. J. Chem. Kinet.*, **10**, 1225 (1978); (d) G. Bartocci, G. Favaro, and P. Bortolus, *Z. Phys. Chem. (Wiesbaden)*, **105**, 13 (1977).

(12) N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, **97**, 2482 (1975).

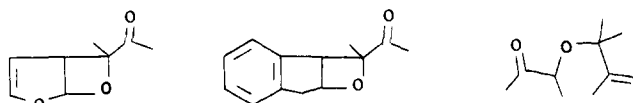
(13) The ionization potential for carefully GLC purified *cis*-DME was checked with reference to a photoelectron spectrum provided by Professor A. D. Baker. Vertical and adiabatic ionization energy values (IP_v = 8.4 and IP_a = 7.7 eV) were quite close to those previously reported.¹² Factors which might make DME an exceptional quencher include a lower steric demand for the enediol ether. We also note that the low-energy photoelectron spectra band for DME is unusually broad (large separation of IP_v and IP_a), suggesting that the quenching act might include a higher degree of distortion for DME than for other quenchers to accompany partial electron transfer. A correlation of quenching constants with adiabatic ionization potentials¹² might have been more satisfactory, but for the varied unsaturated systems employed in our study, a complete set of adiabatic IP values was not available.

Table II. Quantum Yields of Photoaddition and Photoisomerization for Biacetyl and Various Addends

addend	[addend], M	adduct type	ϕ - (additn) ^a	ϕ - (isom)
indene	0.010	BI-IND	0.0067	
	0.017		0.0079	
	0.024		0.0087	
	0.033		0.0094	
	0.052		0.0098	
	0.062		0.010	
tetramethyl- ethylene	0.011	BI-TME	0.046	
	0.022		0.062	
	0.033		0.070	
	0.044		0.072	
	0.055		0.085	
furan	0.100	BI-FUR	0.005	
<i>cis</i> -1,2-dimethoxy- ethene	0.010	BI-DME	0.043	
	0.020		0.030	0.17
	0.030		0.029	
	0.040		0.020	0.14
	0.050		0.019	
	0.060		0.017	0.10
	0.080		0.014	0.090
<i>trans</i> -1,2-dimethoxy- ethene	0.020	BI-DME	0.045	0.048
	0.040		0.033	0.033
	0.060		0.025	0.023
	0.080		0.022	0.019
	0.100		0.019	0.017

^a Quantum yields correspond to disappearance of biacetyl except for DME for which efficiencies refer to appearance of major oxetane, *t*-BI-DME.

gave the oxetanes (BI-FUR and BI-IND) as major products as reported previously.^{2b,c} Biacetyl and TME were not irradiated on a preparative scale but the major products were assumed to be "ene-type" adducts (e.g., BI-TME).^{2b,8} Quantum yields (Table



BI-FUR

BI-IND

BI-TME

II) for biacetyl disappearance in the presence of furan, indene, and TME were measured with the use of a Rayonet chamber photoreactor equipped with lamps with principal emission at 333–390 nm. Plots of reciprocal quantum yield vs. reciprocal alkene concentration were linear and intercept/slope ratios were in agreement with $k_q\tau$ values obtained from phosphorescence quenching (Table I), consistent with the assignment of the biacetyl (n, π^*) triplet as the reactive state. Thus, the data for TME (Figure 2) resulted in $i/s = 78 \text{ M}^{-1}$ ($k_q\tau = 70 \text{ M}^{-1}$) and a limiting quantum yield, $1/i = 0.098$. A similar plot for indene gave $i/s = 133 \text{ M}^{-1}$ ($k_q\tau = 124 \text{ M}^{-1}$) and $1/i = 0.011$. The quantum yield of biacetyl disappearance in the presence of furan was very low, and a complete concentration profile was not obtained. The quantum efficiency was ~ 0.005 at 0.1 M furan, a concentration where biacetyl phosphorescence quenching (but not fluorescence quenching) is nearly complete.

Photoaddition to Dimethoxyethene (DME). Biacetyl and *cis*-1,2-dimethoxyethene (*cis*-DME) on photolysis in benzene or acetonitrile gave two principal products ($\sim 2:1$) which were isolated by preparative GLC and identified by spectral and microanalysis as 1:1 BI-DME oxetane adducts. NMR analysis showed that these GLC purified oxetanes were not homogeneous but in fact consisted of pairs of isomers. Oxetane ring hydrogens for the major photoadduct appeared as two pairs of doublets of unequal intensity ($\sim 5:1$, larger signals at δ 3.8 and 5.0), both pairs of doublets having $J = 3 \text{ Hz}$. A similar spectrum for the minor photoadduct revealed also two pairs of doublets for ring protons (larger component at δ 4.1 and 5.2, $J = 5 \text{ Hz}$). The major adducts were

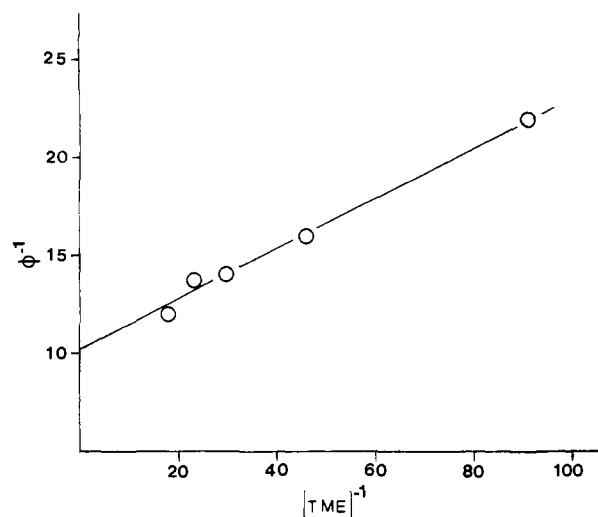
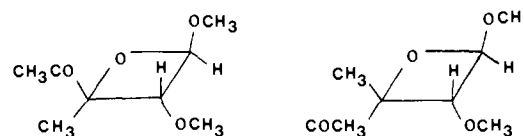
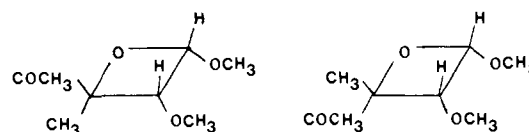


Figure 2. Dependence of quantum yield for disappearance of biacetyl in benzene on the concentration of tetramethylethylene (TME).

assigned epimeric structures having *trans* methoxy groups (*t*-BI-DME) and the minor adducts to the other isomeric pair *c*-

*t*-BI-DME

BI-DME. The assignment relies on the expectation of a higher

*c*-BI-DME

coupling constant for oxetane ring protons which are *cis* oriented, a criterion which has been consistently applied to a number of stereoisomer pairs.^{6,14} Verification of the criterion rests with the assignment of *cis* stereochemistry to the minor adduct of acetone and dimethyl maleate which is alternatively obtained from the adduct of acetone and maleic anhydride.¹⁵

Quantum yields (Table II) for photoaddition of biacetyl as a function of [*cis*-DME] followed a pattern which was different from that observed for the previously described systems. Between 0.001 and 0.01 M DME, the quantum efficiency for appearance of *t*-BI-DME was unchanged (about 0.05) but decreased sharply at higher concentrations. A similar result was obtained starting with biacetyl and *trans*-DME. Two other important features of photolysis in the presence of DME were readily apparent. Geometrical isomerization of the starting alkene accompanied oxetane formation, was somewhat more efficient than cycloaddition, and was also suppressed at high [DME]. Starting with either *cis*- or *trans*-DME, the major oxetane was the *trans* isomeric pair; the ratio of *t*-BI-DME to *c*-BI-DME was $1.62 \pm 0.30:1$ from *cis*-DME and $2.47 \pm 0.45:1$ from *trans*-DME for a wide range of DME concentrations.

The addition quantum yield DME concentration profile was readily analyzed by assuming (1) that oxetane formation is a triplet reaction, (2) that due to the high rate of DME triplet quenching, relatively low concentrations of DME are sufficient to quench virtually all triplets, and (3) that very high concentrations of DME

(14) (a) N. C. Yang, M. Kimura, and W. Eisenhardt, *J. Am. Chem. Soc.*, **95**, 5058 (1973); (b) N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970); (c) J. A. Barltrop and H. A. J. Carless, *ibid.*, **94**, 1951 (1972); (d) G. Jones, II, M. A. Acquadro, and M. A. Carmody, *J. Chem. Soc., Chem. Commun.*, 206 (1975).

(15) E. S. Albone, *J. Am. Chem. Soc.*, **90**, 4663 (1968).

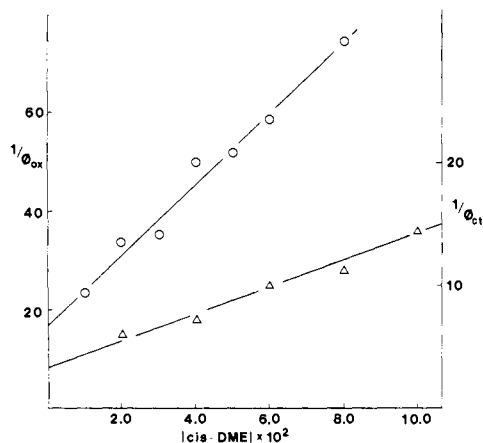


Figure 3. Concentration dependence of reciprocal quantum yields for oxetane formation (O, left ordinate) and trans-cis isomerization (Δ, right ordinate) of biacetyl and *cis*-dimethoxyethene (*cis*-DME) in benzene.

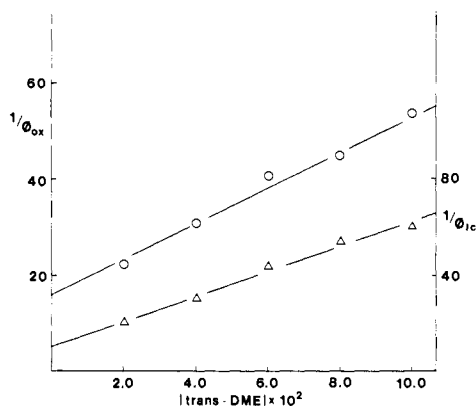


Figure 4. The concentration dependence of reciprocal quantum yields for oxetane formation (O, left ordinate) and trans-cis isomerization (Δ, right ordinate) of biacetyl and *trans*-dimethoxyethene (*trans*-DME) in benzene.

quench biacetyl singlets, thereby reducing the efficiency of addition. If these constraints indeed operate, the quantum yield of product formation (ϕ_{PR}) is simply the product of intersystem crossing yield and the fraction of triplets which lead to a particular product. Thus

$$\phi_{PR} = \left(\frac{k_{isc}}{k_{isc} + k_q^1[DME]} \right) \phi_T \quad (1)$$

$$\frac{1}{\phi_{PR}} = \frac{1}{\phi_T} + \frac{k_q^1[DME]}{k_{isc}\phi_T} \quad (2)$$

where k_{isc} is the rate constant for biacetyl intersystem crossing, k_q^1 is the rate constant for biacetyl singlet quenching by DME, and ϕ_T is the inherent yield of product from biacetyl triplets. (Unimolecular singlet decay other than intersystem crossing is not important.^{1b}) Curved plots of ϕ_{PR} vs. $1/[DME]$ showed that singlet reactivity in cycloaddition and geometrical isomerization is quite low (i.e., from the intercepts, the quantum yields are, conservatively, <0.01 for oxetane formation and geometrical isomerization at infinite concentration of $[DME]$ where all biacetyl decay is bimolecular singlet decay).

Rearrangement of eq 1 reveals a linear relationship of $1/\phi_{PR}$ and $[DME]$ (eq 2). A plot of $1/\phi_{PR}$ vs. $[DME]$ has an intercept = $1/\phi_T$ and a slope/intercept ratio = k_q^1/k_{isc} . The latter should equal $k_q\tau$, values which are alternatively obtained from biacetyl fluorescence quenching. Low conversion quantum yields of *trans*-oxetane appearance and *cis*-*trans* isomerization were obtained starting with biacetyl and *trans*-DME or *cis*-DME; the resulting reciprocal plots are shown in Figures 3 and 4, and the important data are summarized in Table III. Slope/intercept ratios are in reasonable agreement with $k_q\tau$ values obtained from

Table III. Slope and Intercept Data from Plots of Reciprocal Quantum Yield and Dimethoxyethene Concentration (Figures 3 and 4)

	oxetane formatn	geometrical isomerizatn
For <i>cis</i> -DME		
slope	708	110
intercept	17.2	3.10
slope/intercept	41.1	35.6
1/intercept = ϕ_T	0.058	0.322
For <i>trans</i> -DME		
slope	382	510
intercept	15.4	11.1
slope/intercept	24.8	45.9
1/intercept = ϕ_T	0.065	0.107

Table IV. Rate Constant Ratios for Biradical Dynamics (Scheme III) Computed from Product Ratios for Biacetyl/Dimethoxyethene Addition and Isomerization

rate constant ratio	for biradicals (TB)	for biradicals (CB)
$k(\text{cleavage})/k(\text{closure})$	$Z = k_6/k_5 = 5.55$	$Y = k_4/k_3 = 4.12$
$k(\text{closure})/k(\text{rotation})$	$W = k_5/k_2 = 0.055$	$X = k_3/k_1 = 0.025$
$k(\text{cleavage})/k(\text{rotation})$	$k_6/k_2 = 0.305$	$k_4/k_1 = 0.103$

fluorescence quenching by *cis*-DME (30.6 M^{-1}) and *trans*-DME (27.0 M^{-1}). With the assumption of a fluorescence lifetime (τ) of 10.2 ns^2 for biacetyl in benzene, $k_q^1 = 3.0 \times 10^9$ and $2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for *cis*- and *trans*-DME, respectively.

An assessment was made of the effect of solvent on the rate and yield of cycloaddition for biacetyl and *cis*-DME. From results of photolysis in acetonitrile, a linear plot of $1/\phi_{ox}$ (*t*-BI-DME) vs. [*cis*-DME] yielded $s = 317$, $i = 18$, $s/i = 18$, and $1/i = \phi_T = 0.056$. The slope to intercept ratio compared favorably with $k_q\tau = 25 \text{ M}^{-1}$ and $k_q^1 = 3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (assuming $\tau = 8.0 \text{ ns}^2$ in acetonitrile, obtained from fluorescence quenching). The ratio of *t*-BI-DME/*c*-BI-DME was 2.18 ± 0.25 for the photolysis of biacetyl and *cis*-DME in acetonitrile. The *cis*-*trans* isomerization of DME was also observed but not studied in detail.¹⁶

The role of energy transfer in driving the isomerization of DME was evaluated by comparing the effectiveness of biacetyl ($E_T = 56 \text{ kcal/mol}$) and a sensitizer with comparable triplet excitation energy. Thus, parallel irradiation (Rayonet 3000 Å lamps, Pyrex tubes) of 0.01 M DME solutions, nitrogen-purged and 0.2 M in sensitizers biacetyl and 2-acetonaphthone ($E_T = 59 \text{ kcal/mol}$), showed that the latter sensitizer was at least $10\times$ less effective in promoting *cis*-*trans* isomerization of *cis*-DME.

Discussion

Quenching data and concentration profiles for quantum yields are consistent with a predominant role of biacetyl triplets in photoaddition with alkenes.¹⁷ For the addends indene, TME, and furan (and presumably for other alkenes that are not exceptionally good electron donors), the default of singlet reactivity is not necessarily the result of selective bimolecular singlet decay but simply a failure of the alkenes to intercept the shorter lived biacetyl excited state. DME provides a true test of biacetyl singlet and triplet reactivity since both excited states are quenched by the enol ether. Although triplet addition yields ($1/i$ values, Table IV) are moderate, they are (conservatively) fivefold larger than limiting quantum efficiencies for singlet photoaddition. Singlets appear not to play a major role in biacetyl-sensitized alkene isomerization (e.g., *cis*-DME \rightarrow *trans*-DME) as well. A heavy restriction is placed on the triplet mechanism for this reaction since energy

(16) A thorough study with comparable results of photocycloaddition and olefin isomerization and emission quenching for the biacetyl (camphorquinone)/1,2-diethoxyethene systems in acetonitrile has been reported.^{2e}

(17) Photoaddition of biacetyl and DMH² may involve an exceptional mechanism. The quantum yield of adduct formation is low and increases at very high concentrations of DMH. Interpretation of the profile is complicated due to the appearance of an absorbing complex at high [DMH]. Experiments are currently underway to differentiate what appears to be a low residual singlet reactivity⁵ (triplet quenching leads to energy transfer, *vide supra*) from reaction of an excited CT complex.

transfer from relatively low-energy triplets is ruled out (comparison of biacetyl and acetonaphthone).

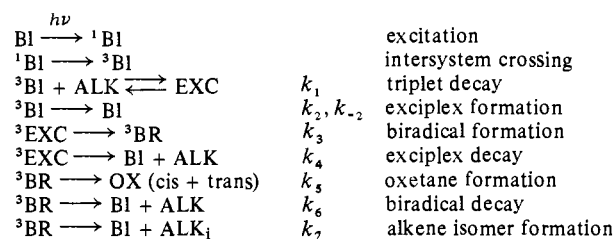
We share the view with others who have studied the stereochemical features of interaction of excited carbonyl triplets and alkenes that oxetane formation and alkene isomerization follow similar paths. Cycloaddition and the accompanying isomerization of alkenes or enol ethers by acetone or benzophenone^{14b,18} have been understood in terms of triplet biradical intermediates which undergo significant stereorandomization before intersystem crossing and cleavage or closure to products. The general observation is partial but not complete convergence of stereochemistries starting with pure alkene stereoisomers, consistent with the findings for the isomerization of simple alkenes sensitized by aryl ketones via the Schenk mechanism.¹⁹

Important questions concerning a photoaddition mechanism involving ketone triplets and biradicals include the following. (1) Are biradicals formed on initial encounter of excited ketone and alkene or do weakly bound excited complexes intervene prior to covalent bonding between the reactive partners? (2) If exciplexes are involved, are they formed irreversibly and do they decay directly to starting addends accounting for a portion of reduced quantum efficiency?

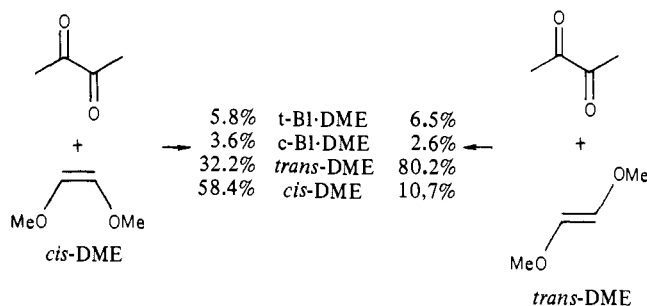
Evidence has been accumulating for some time that the interaction of ketone triplets and alkenes involves exciplex formation. Wagner and Kochevar²⁰ found that the rate of quenching of ketone triplets by alkenes is more responsive to electronic factors (alkene-donor properties) than to steric factors and suggested that direct biradical formation (radical attack on alkene) is not the best model for the structure reactivity relationships observed. This position is relevant to the biacetyl-quenching results, considering particularly the undiminished reactivity of relatively hindered alkenes, TME and hexamethyl(Dewar benzene). Absolute rates of ketone triplet quenching were also judged²⁰ to be unsuitable for the radical addition model being some 2–3 orders of magnitude higher than rates expected for bimolecular reaction of radicals and alkenes ($k = 10^5\text{--}10^7 \text{ M}^{-1} \text{ s}^{-1}$).²¹ This argument seems appropriate for the more robust ketone triplets but is less confidently applied to biacetyl/alkene interactions. Phosphorescence quenching constants are within the range of rates for radical attack, particularly considering that biacetyl triplet may be an exceptionally electrophilic radical.²²

In a separate paper²³ we have discussed the quenching of biacetyl and other ketone triplets by alkenes noting the following features: (1) the regular dependence of quenching constants on the ionization potential of alkene quenchers (for biacetyl, see Figure 1), consistent with the results for other ketones;²⁴ (2) the very wide range of quenching constants for different ketones, employing groups of alkenes having a similar range of electron-donor ability. The latter feature was most apparent in the reduced reactivity of biacetyl triplets. For example, rate constants for quenching acetone and biacetyl phosphorescence by TME are 51^{24} and $6.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively, although the dependence of

Scheme 1



Scheme II



quenching constants on quencher IP for a series of alkenes is similar for the two ketones. The quenching profile was interpreted²³ in terms of reversible formation of triplet ketone/alkene exciplexes, the equilibrium constant for which reflects electron-donor-acceptor (EDA) properties of the quenching partners (Figure 1),²⁵ followed by exciplex decay which in principle involves several paths including formation of biradicals.²⁷

The evidence for formation of triplet ketone/alkene EDA exciplexes parallels the findings for alkene quenching of alkanone and alkanal fluorescence.⁴ Other consistencies noted for biacetyl include the electron-accepting character of biacetyl (n, π^*) singlets^{5,11a} and triplets^{11a} found in general for interaction with a variety of potential electron donors and the general pattern of low reactivity of biacetyl triplets in bimolecular reactions.^{11a,28} The mechanism for quenching of triplet ketones by alkenes is supported by the evidence that an exciplex precursor to biradicals in the acetophenone/2,2-dimethyl-3-hexene system can be intercepted by a secondary quencher.^{19a} In addition, direct evidence for reversible formation of an emitting exciplex for the triplet of the biacetyl relative benzil and an electron donor, anisole, has been obtained.²⁹

The exciplex/biradical mechanism for biacetyl triplet quenching, oxetane formation, and sensitized alkene isomerization is shown in Scheme I. Steady-state analysis gives the relationship below (eq 3) for the quantum yield of oxetane formation where $P = k_5/k_5 + k_6 + k_7$. A similar expression is derived for the quantum yield of alkene isomerization (where $P = k_7/k_5 + k_6$

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(25) Linear free-energy relationships for quenching rate constants (IP plots and the like) are increasingly common and found under circumstances for which the assignment of an outright electron transfer to the quenching mechanism is questionable. For quite a range of electron-donor-acceptor ability in exciplex pairs, electron-transfer (formation of radical ions) is not in evidence and in fact not expected on energetic grounds, and quenching rate constants show a modest dependence on solvent polarity. Exciplex formation and the redistribution of electron density in weak electron-donor-acceptor pairs is the result of a complicated set of intermolecular forces,²⁶ some of which have to do with the mutual polarizability of exciplex participants, thus the correlation with redox thermodynamic parameters and IP's).

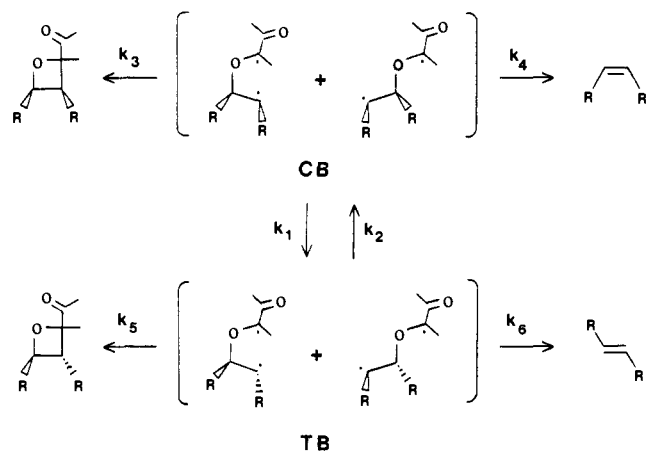
(26) K. Morokuma, *Acc. Chem. Res.*, **10**, 294 (1977), and references cited therein.

(27) Triplet quenching is troublesome since rates of bimolecular decay are generally low enough that a host of chemical paths in principle compete. In the present case, the final chemical result of biacetyl quenching has not been identified for all of the alkenes listed in Table 1, although cycloaddition or the related ene addition reactions are known to be important or can be inferred.²⁸ Hydrogen abstraction to give radical pairs,^{1,8} which may or may not involve the same exciplexes which are employed in addition reaction, is a possible component of quenching for some biacetyl/alkene pairs.

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Scheme III



+ k₇). The intercept/slope ratios (for plots of 1/φ_{ox} vs. 1/[ALK]) and their relationship to phosphorescence quenching constants and biacetyl triplet lifetime (τ = 1/k₁) are shown in eq 3-5.

$$\frac{1}{\phi_{\text{ox}}} = \frac{k_3 + k_4}{Pk_3} + \frac{(k_{-2} + k_3 + k_4)k_1}{Pk_2k_3[\text{ALK}]} \quad (3)$$

$$\frac{i}{s} = \frac{k_2}{k_1} \left(\frac{k_3 + k_4}{k_2 + k_3 + k_4} \right) = k_q\tau \quad (4)$$

$$k_q = k_2 \left(\frac{k_3 + k_4}{k_{-2} + k_3 + k_4} \right) \quad (5)$$

The linear relationship of 1/φ_{ox} and 1/[ALK] is confirmed for biacetyl disappearance in the presence of indene and TME, and quenching constants (k_q) obtained from disappearance quantum yield plots and phosphorescence quenching compare favorably. Association of the triplet exciplex/biradical mechanism with formation of ene products (e.g., BI-TME)⁸ in common with oxetane formation (BI-IND and BI-DME) is warranted in view of results of the labeling study of biacetyl photoaddition to α-methylstyrene.^{2a}

The biacetyl/DME system may be analyzed further by using stereochemical and quantum yield results to analyze exciplex and biradical partition factors which govern quantum efficiencies. Limiting quantum yields (Table II) provide the partition profile for excited BI-DME pairs shown in Scheme II. The analysis of product distributions proceeds, first, by computing relative rates of biradical bond rotation, cleavage, and closure according to Scheme III and by using relative yields of oxetane stereoisomers and "crossover" alkene/oxetane ratios. Next, alkene partition ratios are calculated by using rate constant ratios computed for biradical partitioning in the first step. The analysis shows that the high degree of stereoretention in radiationless decay of BI-DME pairs cannot be accounted for by biradical partitioning and is therefore best attributed to direct decay of an exciplex which is precursor to biradical intermediates. This portion of direct exciplex decay is then computed.

The analysis of biradical kinetics follows the treatment of data for biradicals resulting from diazene decomposition described by Dervan, Uyehara, and Santilli,³⁰ a procedure similar to the early analysis by Montgomery and Bartlett.³¹ Steady-state relationships for the family of biradicals having approximate gauche (nascent cis) stereochemistry for methoxy groups (CB) are readily derived by assuming a start from biacetyl and *trans*-DME (trans biradicals take the symbol TB).

$$\frac{d(\text{CB})}{dt} = k_2(\text{TB}) - (k_1 + k_3 + k_4)(\text{CB}) = 0$$

$$\frac{(\text{TB})}{(\text{CB})} = \frac{k_{-1} + k_3 + k_4}{k_2}$$

Oxetane formation obeys the rate laws.

$$\frac{d(\text{c-BI-DME})}{dt} = k_3(\text{CB})$$

$$\frac{d(\text{t-BI-DME})}{dt} = k_5(\text{TB})$$

Therefore

$$\frac{(\text{t-BI-DME})}{(\text{c-BI-DME})} = \frac{k_5}{k_2} \left(\frac{k_1 + k_3 + k_4}{k_3} \right) = \frac{k_5}{k_2} \left(\frac{k_1}{k_2} + \frac{k_4}{k_3} + 1 \right)$$

Now let

$$\frac{k_5}{k_2} = W \quad \frac{k_3}{k_1} = X \quad \frac{k_4}{k_3} = Y \quad \frac{k_6}{k_5} = Z$$

We use three of these ratios to generate

$$\frac{(\text{t-BI-DME})}{(\text{c-BI-DME})} = W \left(\frac{1}{X} + Y + 1 \right)$$

The oxetane ratio from experiment (starting from *trans*-DME) is 2.47.

A similar treatment of *trans* biradicals at steady state, starting from biacetyl and *cis*-DME, leads to

$$\frac{(\text{c-BI-DME})}{(\text{t-BI-DME})} = \frac{k_3}{k_1} \left(\frac{k_2 + k_5 + k_6}{k_5} \right) = \frac{k_3}{k_1} \left(\frac{k_2}{k_5} + \frac{k_6}{k_5} + 1 \right)$$

$$\frac{(\text{c-BI-DME})}{(\text{t-BI-DME})} = X \left(\frac{1}{W} + Z + 1 \right)$$

The experimental ratio of oxetanes from *cis*-DME is 0.617.

The oxetane stereoselectivity relations yield two equations in two unknowns since cleavage to closure ratios, Y and Z, can be determined directly from product data. Thus, Y = k₄/k₃ = 4.12 is obtained from the ratio of "crossover" (*cis*-DME/*cis*-BI-DME) products resulting from addition to *trans*-DME. Likewise, Z = k₆/k₅ = 5.55, obtained from the *trans*-DME/t-BI-DME ratio for *cis*-DME addition. Solving equations above for the remaining ratios W and X completes the determination of rate constant ratios shown in Table IV. These ratios are now used to compute alkene partition ratios. This step is an attempt to rationalize all limiting quantum yield data, including decay to starting alkene, in terms of biradical partitioning.

For the combination of biacetyl and *trans*-DME

$$\frac{\text{trans-DME}}{\text{cis-DME}} = \frac{k_6(\text{TB})}{k_4(\text{CB})} = \frac{k_6}{k_4} \left(\frac{k_1 + k_3 + k_4}{k_2} \right) = \frac{k_6}{k_2} \left(\frac{k_1}{k_2} + \frac{k_3}{k_4} + 1 \right) = WZ \left(\frac{1}{XY} + \frac{1}{Y} + 1 \right) = 3.31 \text{ (observed 7.50)}$$

For the combination of biacetyl and *cis*-DME

$$\frac{\text{cis-DME}}{\text{trans-DME}} = \frac{k_4(\text{TB})}{k_6(\text{CB})} = \frac{k_4}{k_6} \left(\frac{k_2 + k_5 + k_6}{k_1} \right) = \frac{k_4}{k_1} \left(\frac{k_2}{k_6} + \frac{k_5}{k_6} + 1 \right) = XY \left(\frac{1}{WZ} + \frac{1}{Z} + 1 \right) = 0.462 \text{ (observed 1.81)}$$

The quality of the kinetic analysis above depends of course on the experimental error of product ratios and quantum yields. Thus, the uncertainty in the ratio of oxetane stereoisomers (~20%, from each side) suggests a considerable range for the ratios W and X but leaves unaltered the result that rotation is much faster than closure. Experimental uncertainty associated with the ratio of crossover products will likewise allow variation of Y and Z but the favor for cleavage over closure will remain. Although the comparison of computed and observed alkene ratios depends on absolute quantum yields, we feel confident in claiming a high

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(31) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

similar to the major adduct including the appearance in the NMR spectrum of two components (10:1).

IR (CCl₄): 2920, 1720, 1100 cm⁻¹. NMR (CCl₄): (major component) δ 1.4, 2.2, 3.3, 3.4, 4.1, 5.2; (minor component) δ 1.45, 2.3, 3.9, 5.35 [(assignments in the order given above) for doublets at 3.9, 4.1, 5.2, and 5.35, $J = 5$ Hz]. Analysis was calculated and observed for C and H.

Emission Measurements. The fluorescence of aerated 0.05–0.1 M solutions of biacetyl was monitored at 480 nm in Pyrex cells (excitation at 422 nm). The observation of biacetyl phosphorescence¹¹ required the degassing of samples in cells equipped with ground-glass joints for vacuum line connection (three freeze–pump–thaw cycles). Alternatively, biacetyl phosphorescence was observed from samples fitted with a serum cap and syringe needles for nitrogen purging. The reduction of fluorescence or phosphorescence on the introduction of quenchers was analyzed by using the Stern–Volmer equation $I_0/I = 1 + K_{sv}[Q]$ where I_0 and I are emission intensities without and with quencher and K_{sv} is the Stern–Volmer constant = $k_q\tau$. A linear least-squares program was used to compute the slopes and intercepts of Stern–Volmer plots. Calculated standard deviations were 5% for fluorescence measurements (8–10 points), 20–30% for phosphorescence quenching using the degassing method (4–6 points), and 10–15% using the purging technique (8–12 points).

The lifetime of biacetyl triplet varied according to the technique for oxygen removal and from one run to another. A quantitative measure of this variation was possible on observing the ratio of phosphorescence to fluorescence peak intensities (520 and 480 nm, respectively). This ratio varied between 6–12 using the degassing technique and 12–20 with purging. The assumption was made that fluorescence intensity is a reliable internal standard for phosphorescence yield and that the intensities of the respective emissions at peak maxima reflected relative integrated emission yield. (Biacetyl fluorescence yield was relatively unaffected (<10%) by purging with nitrogen.) The lifetime standard was a value measured recently for similar conditions in benzene at room temperature (135 μ s), for which a phosphorescence/fluorescence peak intensity ratio ($P/F = 12$) was reported.⁸ Lifetimes were therefore calculated for each quenching experiment from P/F ratios before addition of quencher using the formula $\tau = 135/12 \times P/F$. The lifetimes calculated by this method are shown in Table 1. Rate constants from literature quenching data where lifetimes or P/F ratios were not available (indole and norbornene) were computed by using $\tau = 135 \mu$ s.

Quantum Yield Determinations. Solutions (5 ml) containing 0.1 or 0.5 M biacetyl in benzene and varying concentrations of the addends in 15 \times 1.5 cm Pyrex cylindrical tubes were degassed by passing dry nitrogen through syringe needles inserted through rubber serum caps. Tubes were photolyzed in a Rayonet RPR-204 photochemical reactor equipped with a merry-go-round apparatus as described previously.³⁹ The equipment allowed parallel irradiation of biacetyl solutions with varying concentrations of addends and of actinometer solutions for absolute quantum yield measurements. Valerophenone in benzene with dodecane as internal standard was the actinometer (GLC analysis on column B: 5% FFAP, on 60–80 mesh Chrom W, 8 ft \times 1/8 in.), and the conversion to acetophenone was assumed to have a quantum yield of 0.33.⁴⁰ Differential absorption by biacetyl and valerophenone over the emission profile of the Rayonet RUL 3500 lamps was accounted for by using procedures previously described.⁴¹

Biacetyl disappearance on photolysis in the presence of indene, furan, and tetramethylethylene was monitored spectrophotometrically at 422 nm. Photolysis was limited to 20–30% conversion.

Photoproducts from the irradiation of biacetyl and DME were monitored by flame GLC (column B: 20% Carbowax 20 M on 60–80 mesh KOH-washed Chrom P, 10 ft \times 1/8 in.). Formation of *cis*- and *trans*-DME and *c*-B1-DME and *t*-B1-DME was measured vs. an internal standard, dodecane (peak areas corrected for detector response), and conversion to product was limited to <5%.

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Solvent Modified Reactivity of Dimethylsilylene

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Abstract: The insertion of dimethylsilylene into the oxygen–hydrogen single bond of alcohols to yield alkoxydimethylsilanes has been used to probe the effect of solvent on dimethylsilylene reactivity. Competition reactions between pairs of alcohols for dimethylsilylene in various solvents have been carried out. The selectivity of dimethylsilylene is influenced by solvent. Dimethylsilylene is more selective in ether than in hydrocarbon solvents. This difference may result from the formation of complexes between donor solvents and dimethylsilylene. These complexes can deliver dimethylsilylene which is less reactive and more selective than free dimethylsilylene.

Solution of ionic reactive intermediates such as carbocations and carbanions often plays a dominant role in their chemistry.^{1,2} The reactivity of free radicals has also been shown to be sensitive to solvent.^{3–5} While the complexation of carbenes by salts

(carbenoids) in reactions such as the Simmons–Smith reaction has been observed^{6,7} and the existence of transition-metal silylene complexes has been proposed to explain the products of reaction of disilanes catalyzed by these complexes,^{8,9} no effect of solvent

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