Phosphorescence of Substituted Benzophenones in Solution. A Probe of Hydrocarbon Chain Conformation in Three Nonpolar Solvents

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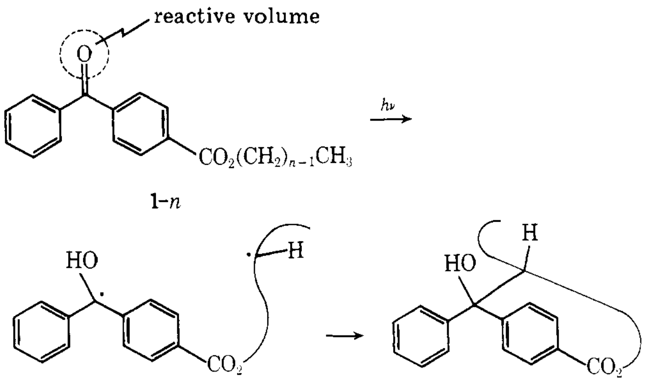
Abstract: Phosphorescence lifetimes are reported for *n*-alkyl esters of benzophenone-4-carboxylic acid, as a function of chain length, for dilute room-temperature solutions in carbon tetrachloride, 1,1,2-trichlorotrifluoroethane (Freon 113), and acetic acid. From these, rate constants, $k_{r,n}$, are obtained for intramolecular emission quenching. Rate constants, k_2, are also obtained for bimolecular quenching by hexane in each solvent. Comparison of $k_{r,n}/k_2 = C_{eff}$ (effective concentration) for the three solvents indicates little, if any, solvent effect on chain conformation. Values of C_{eff} calculated theoretically imply that the chains are flexible and randomly oriented.

This paper presents the results of our study of a photochemical reaction which can be considered to be the macrocyclic analogue of the type II photoreaction. It might also be considered the intramolecular analogue of the reaction between benzophenone triplets and *n*-alkanes. The reaction is the photocyclization of 4-benzoylbenzoate esters, previously exploited for its synthetic utility by Breslow.[1,2] We have undertaken a detailed mechanistic study[3] of this photoreaction in order to develop the reaction into a probe of hydrocarbon chain conformation in solution.

There are two properties of flexible chain molecules which lend themselves to possible theoretical interpretation. One is the mean (or mean-squared) distance of the chain termini. The other is the reversible cyclization probability of the chain.[4] This paper explores photochemical cyclization reactions of long-chain substituted benzophenone derivatives as a means of probing cyclization probability of hydrocarbon chains. While our primary interest is to elucidate the conformation of flexible chains in solution, the thrust of this paper is to describe the spectroscopy and photochemistry of our probe, **1**.

The fundamental concept underpinning this research is that the rate constant for intramolecular hydrogen abstraction in **1** is proportional to the probability P_n that a chain element occupies the reactive volume about the reactive carbonyl during the lifetime of the excited state. The chain-length dependence of this rate constant, $k_{r,n}$, would probe the chain-length dependence of the cyclization probability P_n of an *n* carbon chain. The solvent dependence of these rate constants might probe solvent effects on chain conformation.



1-*n*

2

3

Breslow[1] has studied aspects of the photochemistry of **1**. If the reaction to form **3** were quantitative, and if reactions leading to analysis of oxidation sites in **3** were quantitative, information about the conformation of the chain could be obtained from his experiments. Similar information could be obtained if one could assume that partitioning among products were not sensitive to the site of oxidation along the chain. It is not clear that the assumption is valid. We have, however, found general agreement between Breslow's data[1] and our lattice-walk Monte Carlo calculations of cyclization probabilities in **1**.[5]

Results

All of the esters **1** had identical absorption spectra. The corresponding emission spectra in degassed room temperature solution were identical in shape, but decreased in intensity as the chain length increased. Spectroscopic data for these compounds are presented in Table I.

Phosphorescence lifetimes of these benzophenonecarboxylate esters were both solvent and chain-length dependent. Within any one solvent the emissive lifetimes in fluid solution were approximately the same for the methyl, propyl, and pentyl esters. The propyl and pentyl esters were very difficult to purify. For chain lengths longer than $n = 9$, the measured lifetimes decreased with increasing chain length. These data are presented in Figure 1. These triplet lifetimes were independent of concentration over the range 3×10^{-4} to 5×10^{-3} M; so, too, were the quantum yields of phosphorescence, ϕ_p. The phosphorescence quantum yields (see Figure 2) were sensitive to solvent and chain length in a manner exactly paralleling the behavior of the triplet lifetimes. Values of ϕ_p were unaffected within experimental error (±10%) by change of excitation wavelength from 345 to 320 nm.

Product Quantum Yield Measurements. Quantum yields were determined for disappearance of starting material, for esters of varying chain lengths, in carbon tetrachloride solution. Quantum yields for disappearance of starting material [ϕ_{diss}] had to be measured under conditions identical with those for lifetime measurements, in order to be certain that bimolecular processes made no contribution to the observed reactions. These conditions involved sufficiently dilute solutions that standard merry-go-round devices were inappropriate. Samples absorbed only a fraction of the incident light. Careful monitoring of the change of absorbance with time was necessary.

The approach of Johns[5] lends itself to determining quantum yields under such circumstances. Here one determines the absorption cross section σ_a and the photochemical reaction cross section σ. The former, $\sigma_a = 2.3 \times 10^{-3}\epsilon_\lambda$, where ϵ_λ is the

Table I. Spectroscopic Data for Esters[a] of Benzophenone-4-carboxylic Acid

	CCl_4	Freon 113	HOAc
	Absorption[b]		
λ_m (S_1, $n\pi^*$)	336 sh, 346, 355 sh[c]	345	341
ϵ	183, 201, 183	162	192
λ_m (S_2, $\pi\pi^*$)	256	283 sh; 252	254
ϵ	25 000	10 300; 31 100	24 100
	Emission[b]		
T_1 (0,0)	432.5	430.0	434.5
T_1 (0,1)	463.0	460.5	462.0
T_1 (0,2)	494.5	490.0	492.0

[a] These specific measurements are for the methyl ester, **1**-1. [b] Absorption maxima and emission bands are given in nm; emission spectra are uncorrected. [c] Shoulder.

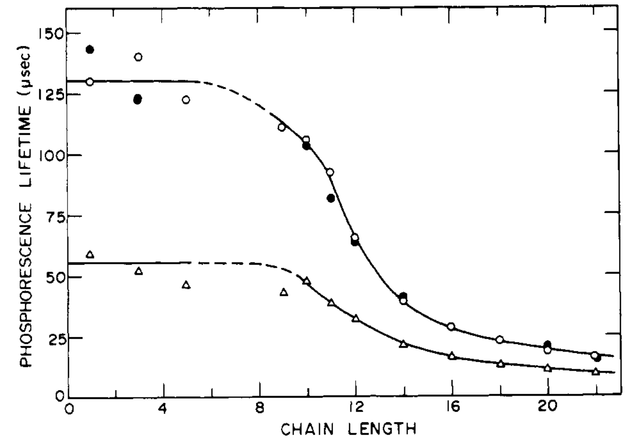


Figure 1. Phosphorescence lifetimes of the esters **1** as a function of chain length in three solvents: CCl_4 (○), Freon 113 (●), and acetic acid (△).

molar extinction coefficient of the sample at wavelength λ. The photochemical quantum yield is given by eq 1. Since ϵ_λ is the same for all the esters, the σ_a values are identical. Relative quantum yields are determined by eq 2.

$$\phi_{\text{diss}} = \sigma/\sigma_a \tag{1}$$

$$\phi_{\text{diss}(n=i)}/\phi_{\text{diss}(n=j)} = \sigma_{n=i}/\sigma_{n=j} \tag{2}$$

In actual practice, photochemical reaction cross sections were determined for all esters relative to that of **1**-16, arbitrarily chosen as a standard. Irradiations were carried out in matched cells on an optical bench. Disappearance of the benzophenone chromophore was monitored by uv spectrometry. At the end of these experiments, the quantum yield for reaction of **1**-16 was similarly determined to be $\phi_{\text{diss}} = 0.12$ by ferrioxalate actinometry. The data are presented in Figure 3.

Bimolecular Quenching. Rate constants for bimolecular quenching, k_2, of benzophenone and 4-carboxymethylbenzophenone were determined in each solvent for *n*-hexane, cyclohexane, and 2-propanol. Rate constants were obtained from the modified Stern-Volmer expression

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_2[\text{RH}] \tag{3}$$

where τ is measured phosphorescence lifetime, and τ_0 is that in the absence of quencher RH. For a number of examples, the standard Stern-Volmer expression (4) gave identical (but less precise) values for k_2 from emission intensity measurements.

$$I_0/I = 1 + k_2\tau_0[\text{RH}] \tag{4}$$

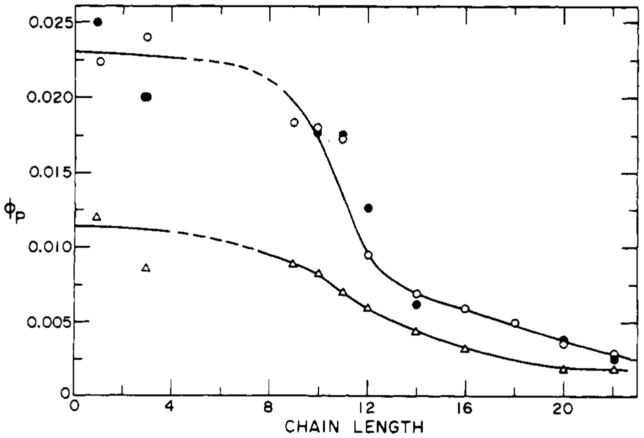


Figure 2. Quantum yields of phosphorescence, ϕ_p, for the esters **1** as a function of chain length in three solvents: carbon tetrachloride (○), Freon 113 (●), and acetic acid (△).

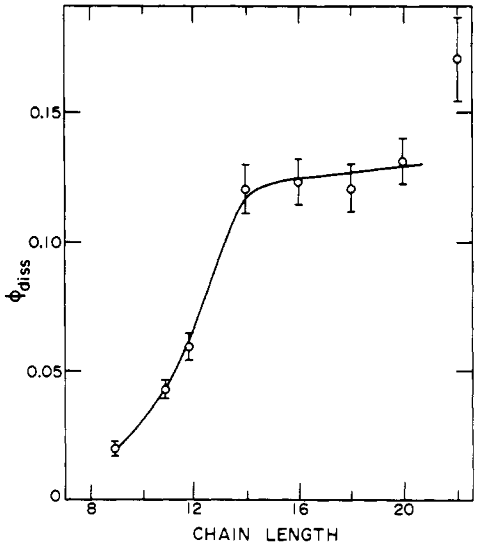


Figure 3. Quantum yields for disappearance of **1** in carbon tetrachloride as a function of chain length. Error bars are one standard deviation and are determined by the standard error in calculating the photochemical cross section σ.

Table II. Bimolecular Rate Constants for Various Quenchers in Acetic Acid, Carbon Tetrachloride, and Freon 113[a]

		$10^{-5}k$, $M^{-1}\,s^{-1}$			
Solvent	Ketone	Hexane	Cyclohexane	2-Propanol	Naphthalene
Acetic acid	Benzophenone	3.51	10.0	7.4	
	1-1	6.82 6.97[b]	14.1	16.2	55 700
Carbon tetrachloride	Benzophenone	2.91	8.8		
	1-1	4.81 5.37	11.9	59	
Freon 113	Benzophenone	3.70		16.4	
	1-1	4.17 4.25 3.96	8.39	37.2	91 200

[a] Rate constants are obtained from eq 7. [b] Where more than one value of k_2 is reported, the latter values were obtained using different preparations of alkane, solvent, and ketone.

2-Propanol was fractionally distilled through a 24-in. Vigreux column. A center cut was used. n-Hexane and cyclohexane, 99+ mol %, were stirred with up to half their volume of sulfuric acid, under nitrogen, with successive changes of acid until the sulfuric acid layer remained colorless. After an aqueous workup, these alkanes were distilled and stored under nitrogen. GLC analysis showed less than 0.001% alkene.

Quencher purity is a key concern. For example, we obtained k_2 for a sample of n-pentane quenching benzophenone emission in carbon tetrachloride. This sample was later found to contain 0.002% 2-methyl-2-butene. From data reported by Cohen[6a] and Wagner,[6b] we estimate that this impurity contributes 5% to the value of $k_2 = 2.1 \times 10^5$ M^{-1} s^{-1} calculated from eq 3. Steel has discussed this problem in some detail.[7] Since many of our conclusions are critically dependent upon confidence in these k_2 values, we took pains to explore the reproducibility of these values for different preparations of ketone, alkane, and solvent, and even for the possibility of experimenter bias. These values are tabulated in Table II. From these data we estimate the precision in k_2 to be ±5%.

Results that led Lewis to suspect that high-purity 2-propanol may contain a trace of quenching impurity[8a] have recently received an alternative interpretation.[8b]

Discussion

It is clear from the data in Figure 1 that chains shorter than nine carbons cannot quench emission, intramolecularly, from the excited benzophenone. We infer that chains must reach the ketone carbonyl oxygen to quench emission. Space-filling molecular models confirm this prediction for the ester group fixed in the trans coplanar conformation.

Our ultimate intent is to derive information about the conformation of hydrocarbon chains in various solvents from investigation of the kinetics of photochemical reactions of **1** and its derivatives. To interpret rate constants, one needs to assume a reaction mechanism. Furthermore, one needs to take some pains to establish that *those aspects* of the mechanism, from which conclusions will be drawn, are indeed correct.

We take as our working hypothesis, the mechanism of the photoreaction of **1**-n outlined in Scheme I. Irradiation of **1** gives the singlet state ^{1}**1*** which decays radiationlessly to give the triplet state ^{3}**1*** with unit efficiency.

The triplet ^{3}**1*** can emit a photon (phosphoresce) with a rate constant k_p. It has many chain-length-independent, first-order, radiationless processes for decay to the ground state. These include internal conversion, energy transfer to solvent, and quenching by trace impurities in the solvent. They are summed and assigned the first-order rate constant k_d. This rate constant has no theoretical significance. It serves only as a useful measure of solvent purity.

When the chain is long enough, a new radiationless process becomes manifest. It is assigned the rate constant $k_{r,n}$ to indicate that its magnitude is chain-length dependent. It probably describes hydrogen abstraction from the chain. For the sake of rigor we will call $k_{r,n}$ the rate constant for intramolecular emission quenching. We assume that each unactivated CH_2 group contributes to intramolecular quenching, depending upon its ability to reach the ketone carbonyl. Therefore, $k_{r,n}$ reflects a summation of quenching reactions over the $(n - 1)$ methylenes, eq 5. The methyl group is not reactive under our conditions.[1]

$$k_{r,n} = \sum_{i}^{n-1} k_{r,i} \qquad (5)$$

Since $k_{r,n}$ is proportional to P_n, the probability that a CH_2 group occupies the reactive volume about the ketone carbonyl oxygen, determination of this rate constant will be the focus of our interest. It is not crucial, from a conformational point of view, whether $k_{r,n}$ describes hydrogen abstraction or some more peculiar[9] quenching process; neither, for that matter, are questions relating to the partitioning of the biradical species. These are important *photochemical* questions. We will discuss them in turn at the end of this paper.

The rate constants $k_{r,n}$ are obtained as follows: The reciprocal lifetime $\tau_n^{-1} = k_p + k_d + k_{r,n}$. For short chains, $k_{r,n} = 0$. If k_p is a function only of the chromophore, and k_d is a function only of chromophore and the solvent, then, for short chains, e.g., **1**-1, $\tau_1^{-1} = k_p + k_d$. One can obtain $k_{r,n}$ by doing the subtraction indicated in eq 6. These data are presented in Table III.

$$\frac{1}{\tau_n} - \frac{1}{\tau_1} = k_{r,n} \qquad (6)$$

Both assumptions in the preceding paragraph can be tested. From the relationship ($\phi_{p,n} = k_p\tau_n$) one can calculate k_p from measured values of ϕ_p and τ from the same sample tube. In carbon tetrachloride, $k_p = 182 \pm 13$ s^{-1}; in Freon 113, $k_p = 180 \pm 15$ s^{-1} in acetic acid, $k_p = 195 \pm 15$ s^{-1}. From the data in Figure 1, it is clear that $\tau_1^{-1} \approx \tau_3^{-1} \approx \tau_5^{-1}$. Since k_p values are constant, and $\tau^{-1}{}_{n<9} = k_p + k_d$, the k_d values are constant in any one batch of solvent.

The most serious prediction of the mechanism outlined in Scheme I is that τ_n, but not $k_{r,n}$, should be very sensitive to solvent purity. Changes in solvent purity should be reflected

Scheme I

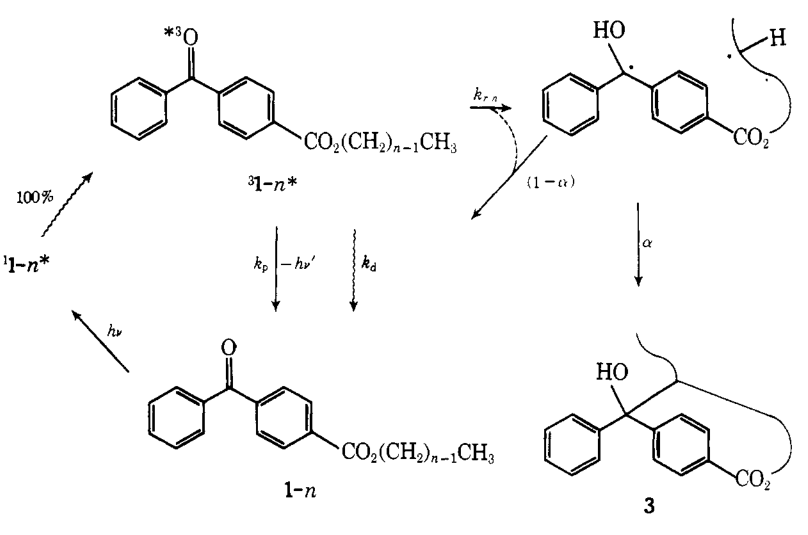


Table III. Phosphorescence Lifetimes, τ_n, and Intramolecular Quenching Rate Constants, $k_{r,n}$, in Carbon Tetrachloride, Acetic Acid, and Freon 113

n:	1	3	5	9	10	11	12	14	16	18	20	22
					Carbon Tetrachloride[a]							
τ_n, μs	128	140	120	110	105	92.3	64.2	38.7	27.8	22.9	18.4	16.6
$10^{-3}k_{r,n}$, s^{-1}	0	0	0	1.3	1.7	2.9	7.8	18.0	28.2	35.8	46.5	54.3
					Acetic Acid[a]							
τ_n, μs	59.0	51.9	46.4	42.6	48.0	38.0	30.9	19.5	14.5	12.2	9.7	8.6
$10^{-3}k_{r,n}$, s^{-1}	0	0	0	0	3.8	9.3	15.4	34.2	52.0	65.0	86.1	99.3
					Freon 113[a]							
τ_n, μs	143	122			104	81.4	64.1	38.8			18.3	16.1
	63.3[b]								20.7	17.1		
$10^{-3}k_{r,n}$, s^{-1}	0	0			2.6	5.3	8.7	18.5	32.5	42.5	47.6	55.5

[a] All experiments were carried out in a single batch of purified solvent except where noted. [b] Second batch of solvent.

Table IV. τ_n and $k_{r,n}$ Values in Carbon Tetrachloride

		Chain length		
		1	14	18
Batch A (k_d = 7300 s^{-1})	τ_n, μs	128	38.7	22.9
	$k_{r,n}$, s^{-1}		18 000	35 800
Batch B (k_d = 64 000 s^{-1})	τ_n, μs	15.7	12.25	10.1
	$k_{r,n}$, s^{-1}		18 000	35 000

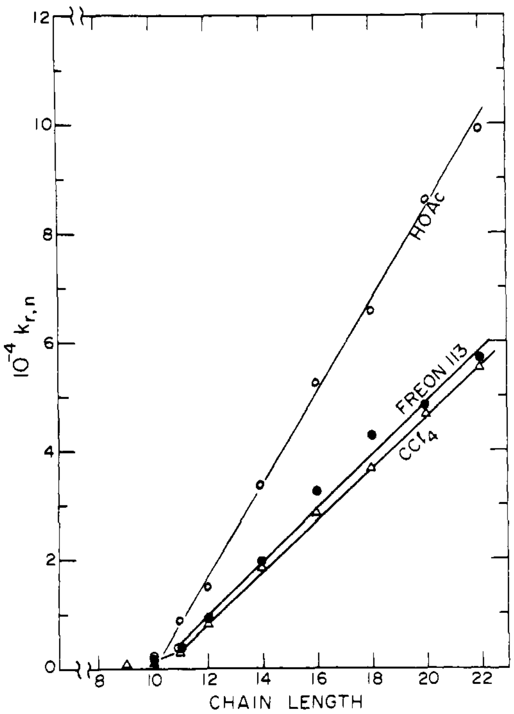


Figure 4. Values of the rate constant $k_{r,n}$ as a function of chain length in **1** in three solvents: CCl$_4$ (△), Freon 113 (●), and acetic acid (○).

in different values for k_d. These predictions were tested on a partially purified batch of carbon tetrachloride, for which τ_1 was only 15.7 μs. These results are presented in Table IV. The agreement in $k_{r,n}$ values lends strong support to the mechanism given in Scheme I.

Intramolecular Quenching and Solvent Effects. Values of $k_{r,n}$ are plotted against n in Figure 4 for the three solvents: acetic acid, carbon tetrachloride, and Freon 113. While $k_{r,n}$ values in Freon 113 are very close to those in CCl$_4$, $k_{r,n}$ values in acetic acid are larger by a factor of 1.8.

Freon 113 is a highly chlorinated fluorocarbon. It is not surprising that its properties toward intramolecular quenching resemble those of carbon tetrachloride. Acetic acid exists in solution as a dimer. It has a very low dielectric constant (ϵ = 6).[10] Perhaps because it is protic, it is a reasonable solvent for ions. It causes a very large blue shift in the $S_0 \rightarrow S_{n\pi^*}$ maximum for both benzophenone[11] and **1**.

The increased values of $k_{r,n}$ in acetic acid might have two sources. Acetic acid might perturb the conformation of the hydrocarbon chain in such a way as to increase the cyclization probability P_n. On the other hand, there might be a solvent effect on the rate constant for emission quenching of ^{3}**1*** by an unactivated methylene. To choose between these possibilities, one must examine a bimolecular analogue of the emission quenching process. We have chosen n-hexane as a model for a flexible unactivated hydrocarbon chain. We have determined its rate constant, k_2, for quenching the emission of the methyl ester **1**-1 in carbon tetrachloride, Freon 113, and acetic acid. These data are presented in Table II.

The ratio of k_2(HOAc)/k_2(Freon 113) = 1.7. The ratio of k_2(HOAc)/k_2(CCl$_4$) = 1.4. Much of difference in $k_{r,n}$ values in these solvents is explained by a solvent effect on the triplet quenching process. To the extent that emission quenching by hexane is a good model for the intramolecular quenching reaction described by $k_{r,n}$, one can conclude that Freon 113 and acetic acid have the same effect on the cyclization probability of the chain.

Differences remain in the $k_{r,n}/k_2$ ratios, between carbon tetrachloride on one hand, and Freon 113 and acetic acid on the other. These differences are small, about 15–20%, which is outside of experimental error for the ratio of two k_2 measurements. These differences may reflect a small, real perturbation of the solvent on the chain conformation, or they may be dependent on the choice of hexane as the bimolecular model for the emission quenching reaction.

Quantitative Aspects of Chain Conformation. The rate constant, $k_{r,i}$, for emission quenching by the ith CH$_2$ group in an n carbon chain is proportional to the probability P_i that it occupies the reactive volume about the ketone oxygen during the lifetime of the excited state. The calculated experimental rate constant $k_{r,n}$ is equal to the sum of contributions of each of the (n − 1) CH$_2$ groups in the chain. The total cyclization probability P_n is similarly equal to the sum of probabilities that each CH$_2$ group occupies the reactive volume.

$$k_{r,n} = \sum_{i=1}^{n-1} k_{r,i} \propto P_n = \sum_{i=1}^{n-1} P_i \tag{7}$$

Equation 7 is true regardless of the factors influencing P_n. A conformational analysis of flexible chains involves determining these factors. Our approach is to develop theoretical methods for calculating P_n from various models of chain behavior and compare these with experimental values of $k_{r,n}$.

The model we have chosen to explore first is that of random chains (with tetrahedral bond angles) in a neutral solvent. A neutral solvent, which differs from Flory's θ-solvent, is one in which the hypothetical heat of mixing of the chain repeat-unit with the solvent is zero. In other words, such a solvent does not perturb the chain from conformations dictated by its own rotational isomeric energies, and its steric and excluded volume requirements.

We have developed Monte Carlo methods, based on a diamond-lattice random walk model with second neighbor exclusions, for estimating cyclization probability.[4] This model takes complete account of steric and excluded volume effects. Among its weaknesses are the assumptions of hard-sphere nonbonded repulsions and exaggerated C–H bond lengths.[4] Fortunately these have offsetting effects. These calculations are best described as computer-based molecular models, with which one can estimate the number of reactive conformations and number of total conformations of an n carbon chain. Using this model, we can estimate P_n [P_n = (reactive conformations)/(total conformations)] for chains random in orientation within the stricture of tetrahedral bond angles. For the sake of simplicity, in this paper we consider the reactive volume about the ketone oxygen in **1** to be spherical.

The most simple test of whether the hydrocarbon chains in **1** behave as random, flexible chains in a neutral solvent is to examine whether $k_{r,n}$ values in real solvents are proportional to calculated values of P_n.

Values of P_n are compared with $k_{r,n}$ obtained in acetic acid in Figure 5, and with $k_{r,n}$ obtained in carbon tetrachloride in Figure 6. In both solvents, the criterion of proportionality is observed. While it is somewhat satisfying to see this initial hypothesis confirmed, this criterion is not very stringent. Only gross solvent effects on structure might be detected.

A more stringent test would be the direct calculation of the ratio $k_{r,n}/k_2$ from P_n, since the former ratio should reflect only conformational properties of the chain. It should be obvious from the data in Figures 5 and 6 that $k_{r,n}/k_2$ is proportional to P_n.

The ratio $k_{r,n}/k_2$ has units of molarity. We define this ratio as the effective concentration, C_{eff}.[12] The concept of effective concentration has been applied to a number of systems, particularly in the field of models for enzyme-catalyzed reactions.[13] The interpretation of C_{eff} as a true "local" concentration, namely the probability (in moles) of a species occupying a volume (in liters) about some part of a molecule, is least ambiguous when two criteria are met: (a) The corresponding bimolecular reaction is slower than diffusion controlled. (b) Special effects, particularly relief of steric strain, which forces reactive groups into proximity, are absent. Factors like relief of steric strain in reactions proceeding through small rings often give values of $C_{\text{eff}} > 100$ M.[13] We put forth the point of view that only when C_{eff} is smaller than or equal to concentrations at which the bimolecular reaction rate depends linearly on concentrations (and its activity coefficients are 1.0), is C_{eff} interpretable as a time-averaged local concentration. This is likely to be the case for $C_{\text{eff}} < 10^{-1}$ M.

For point (a) to hold, a conformational equilibrium must precede the reaction. C_{eff} has no meaning as a time-averaged concentration if it describes a diffusion controlled reaction. This argument has been developed in detail by Morawetz.[12]

$$C_{\text{eff}} = \frac{P_n/N_A}{V} = \frac{397P_n}{r^3} \tag{8}$$

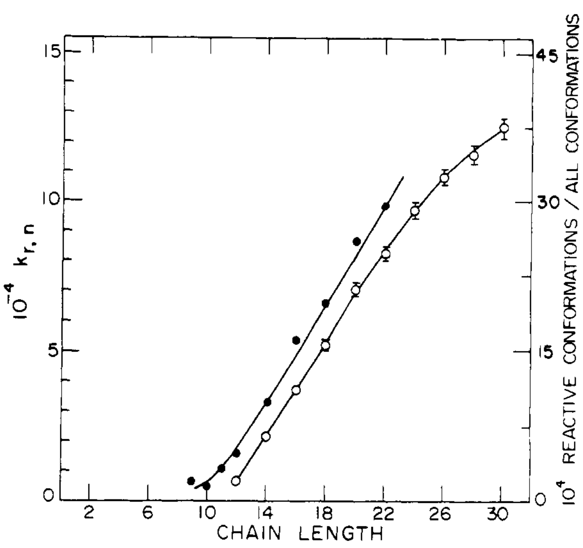


Figure 5. Values of the rate constant $k_{r,n}$ in acetic acid (left ordinate), and of the theoretical cyclization probability P_n (right ordinate), as a function of chain length. Error bars are one standard deviation.

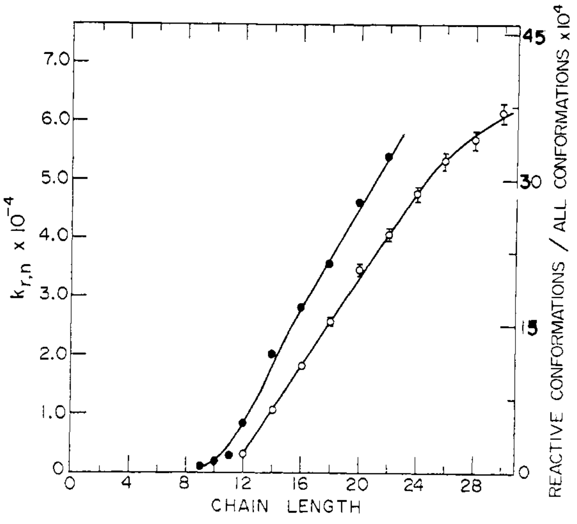


Figure 6. Values of the rate constant $k_{r,n}$ in carbon tetrachloride (left ordinate), and of the cyclization probability P_n (right ordinate), as a function of chain length. Error bars are one standard deviation.

According to Morawetz,[14] the effective concentration can be related directly to the probability of finding a particle in a volume. In eq 8 P_n represents the probability of finding a hydrogen from a CH_2 group in the reactive volume V about the ketone carbonyl oxygen. P_n/N_A (N_A is Avogadro's number) is the number of moles of methylenes in that volume. If the appropriate values are substituted into eq 8, $C_{\text{eff}} = 397P_n/r^3$, where r is the radius (in angstroms) of the reactive sphere about the ketone carbonyl oxygen. A quantitative description of hydrocarbon chain conformation would compare experimental determinations of C_{eff} with those calculated theoretically for suitable models of chain conformation.

Our previous calculations of P_n have ignored the energy biasing gauche and trans rotamers of the chain. We have recently learned to store on tape the step weights and coordinates of both reactive and unreactive chains. Using an appropriate algorithm, we reweight each gauche step by a factor of $\exp(-\Delta E/RT)$, where ΔE is chosen as 0.5 kcal/mol. This procedure is rather complex and will be described separately. Preliminary results[15] suggest that the general shape of the P_n vs. n plot is not significantly affected by temperatures as low as 25°, and, furthermore, temperature effects on the magnitude of P_n, over the same temperature range, are exceedingly small. The error bars in P_n at 25° are rather large (±10%). We prefer, at this time, to confine our discussion to comparison of

Table V. Experimental Values of Effective Concentration

	C_{eff}, M		
n	CCl_4	Freon 113	Acetic acid
9	0.0025		
10	0.0034	0.0064	0.0056
11	0.0058	0.013	0.014
12	0.015	0.021	0.022
14	0.035	0.046	0.050
16	0.056	0.078	0.075
18	0.071	0.10	0.094
20	0.090	0.12	0.13
22	0.11	0.14	0.14

Table VI. Calculated Values of the Cyclization Probability, P_n, and Effective Concentration for Various Reactive Radii[a,b]

		C_{eff} (calcd)[d]		
n	$10^4 P_n$	$r = 1.8$ Å	$r = 1.9$ Å	$r = 2.0$ Å
12	1.81 ± 0.06[c]	0.012	0.010	0.009
14	6.2 ± 0.1	0.041	0.035	0.030
16	10.7 ± 0.2	0.073	0.062	0.053
18	15.8 ± 0.2	0.11	0.091	0.073
20	20.7 ± 0.2	0.14	0.12	0.10
22	25.2 ± 0.2	0.18	0.15	0.13
24	28.9 ± 0.2	0.20	0.17	0.15

[a] Numerical calculations carried out assuming ΔE(trans-gauche) = 0; see text. [b] The reactivity of the carbonyl *oxygen* in ^{3}**1**-n is taken to be spherically symmetric; i.e., reactions are counted for CH_2 groups occupying any of the three lattice sites adjacent to this oxygen in the model. See ref 4. [c] One standard deviation. [d] Reactive radius in angstroms.

experimentally obtained values of C_{eff} with those obtained from our previous calculations. Values of P_n and corresponding values of C_{eff} calculated from various values of r are presented in Table VI. These may be compared with experimental values of C_{eff} listed in Table V.

Obviously, from the data presented previously in Figures 5 and 6, there is some value r for which the calculated and experimental values of C_{eff} agree. To assert that hydrocarbon chains in acetic acid, Freon 113, and carbon tetrachloride behave quantitatively as though they are randomly oriented and freely flexible, we should find a value of r which is chemically meaningful. A chemically meaningful value of r should be no smaller than the O-H bond length, nor larger than the sum of the van der Waals radii of H in CH_2 and O in C=O. This value is 2.5 Å.[16] The dashed line in Figure 7 represents C_{eff} for $r = 2.0$ Å with P_n calculated as reported previously. The experimental data are accommodated by the model of flexible and random chains for values of r between 1.8 to 2.2 Å. Within the limitations of the model, we assert that hydrocarbon chain conformations in these three solvents are quantitatively described by a model which assumes random, flexible behavior.

Solvent Effects and Substituent Effects on Bimolecular Quenching Reactions. Radical hydrogen abstraction from alkanes and benzophenone triplet quenching by alkanes have many features in common. To a first approximation, one would not expect significant solvent effects on hydrogen abstraction reactions from alkanes, unless the solvent complexed the attacking radical species.[17] There are allusions in the literature to polar effects in hydrogen abstraction reactions,[18] but no firmly documented examples for alkanes. Steel has found similar rate constants for benzophenone quenching by several alkanes in acetonitrile and carbon tetrachloride.[17]

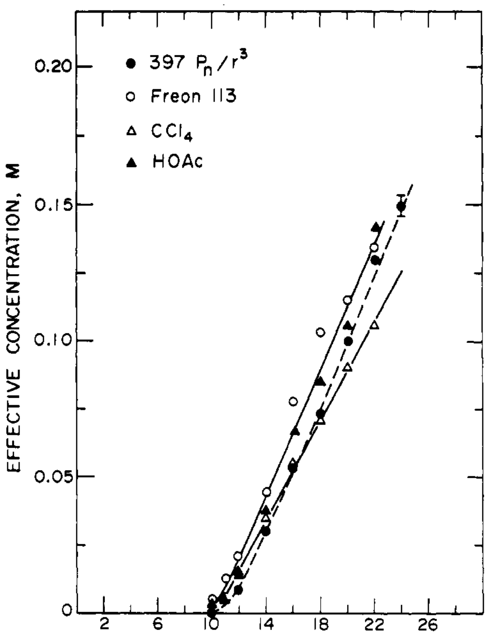
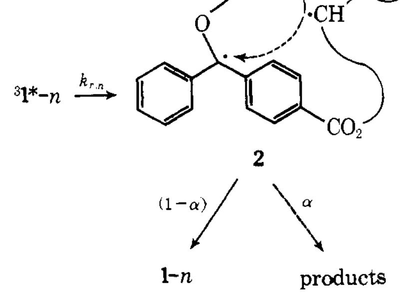


Figure 7. Effective concentration as a function of chain length. Solid lines represent values calculated from $k_{r,n}/k_2$. Dashed line derives from P_n, calculated for a reactive radius $r = 2.0$ Å. Error bar is one standard deviation.

We have examined quenching of both benzophenone emission and that of its 4-carboxymethyl derivative **1**-1 by hexane, cyclohexane, and 2-propanol. These have been examined in acetic acid, carbon tetrachloride, and Freon 113. The data are presented in Table II. Solvent effects are, for the most part, small, but significant. We find no obvious trends to these data.

There is a substituent effect on emission quenching, consistent with the observations of Yang and Dusenbery.[19] They report that electron-withdrawing substituents in the para position of substituted benzophenones increase k_2 values for 2-propanol in benzene. Wagner also has observed that electron-withdrawing substituents on the aromatic ring of valerophenone increase the rate constant for the type II photoreaction.[20] The substituent effects observed here are larger for reaction with 2-propanol than for reaction with the alkanes.

Fate of the Biradical Intermediate. If the mechanism of intramolecular triplet quenching in **1** involves only hydrogen abstraction, then data obtained in this work allow us some insight into the partitioning of the biradical intermediate in the photochemical reaction of **1** between products and starting material. By making this assumption, we can describe the quantum yield for formation of products, $\phi_{diss} = \alpha_n k_{r,n} \tau_n$. The



product $k_{r,n}\tau_n$ represents the quantum yield of biradical formation; α_n describes the fraction of **2** which goes on to form products. Values of α_n calculated in this manner are presented in Table VII.

Table VII. Quantum Yields for Disappearance of Starting Material and Partitioning[a] of the Biradical Intermediate in Carbon Tetrachloride

	Chain length								
	9	11	12	14	16	18	20	22	Av
$\phi_{diss}{}^{b,c}$	0.02	0.043	0.063	0.12	0.12	0.12	0.13	0.17	
$k_{r,n}\tau_n$	0.14	0.27	0.50	0.70	0.78	0.82	0.86	0.90	
$\alpha_n{}^b$	0.14	0.16	0.13	0.17	0.15	0.15	0.15	0.19	0.16

[a] Presumes quenching involves hydrogen abstraction (see text). [b] Estimated error ±10%. [c] Quantum yield for disappearance of starting material.

The most surprising aspect of the data in Table VII is the apparent chain-length independence of α_n. These values of α represent contributions from each of the sites of hydrogen abstraction along the chain. As such, α is difficult to interpret. One can, however, state that on the average in carbon tetrachloride at room temperature, the biradicals **2** disproportionate to starting material 5.7 times as often as they cyclize to form product.

Experimental Section

Carbon tetrachloride (Fisher spectral grade) and 1,1,2-trichlorotrifluoroethane (Freon 113, MCB spectral grade) were purified by Schuster's method.[21] Reagent grade acetic acid (Corco Chemical) was refluxed over 2% chromium trioxide for 10 h. It was then distilled and finally fractionally distilled.[22]

Benzophenone was BDH reagent grade purified by sublimation, recrystallizing twice from hexane, followed by sublimation. 4-Benzoylbenzoic acid (Aldrich) and the various alkyl halides (Eastman-Kodak) were used for the synthesis of the alkyl esters of 4-benzoylbenzoic acid without further purification.

Purification of Cyclohexane, *n*-Hexane, Naphthalene, and 2-Propanol. Fisher spectral grade cyclohexane (300 ml) was stirred with about 25 ml of concentrated sulfuric acid under nitrogen for 24 h, washed four times with 25 ml of saturated sodium bicarbonate, and washed five times with 50 ml of distilled water. It was then dried over anhydrous magnesium sulfate and distilled fractionally through a Vigreux column. Olefinic impurities were detected by gas chromatography using a 5 ft × 0.125 in. o.d. silver nitrate-glycerol column. Hexane was examined on a 5 m × 0.125 m o.d. column.

The column was prepared by Bendas' method.[23] Silver nitrate (60 g) was ground to powder and was then added, 1 g at a time, to 40 ml of glycerol stirred rigorously in a beaker. When all the powdered silver nitrate had been added, the resulting mixture was stirred for an additional 0.5 h. The saturated solution was centrifuged and the undissolved silver nitrate was separated. A 34-ml portion of this saturated solution was then added to 79.5 g of Chromosorb P (80-100 ml) and the mixture was shaken for about 10 min. To this mixture, about 200 ml of ACS methanol was added (this represents a modification of Bendas' technique). A homogenous mixture was obtained by removing the added methanol on a rotary evaporator. The purified cyclohexane showed the absence of olefins to the limit of 0.001%.

BDH reagent grade *n*-hexane was purified similarly and showed only 0.0006% olefin impurity.

Electrograde 2-propanol from Fisher was found to contain less than 0.01% impurities by a Carbowax column in gas chromatography. It was fractionally distilled.

BDH naphthalene was purified by recrystallizing three times in hexane.

Synthesis of 4-Carboxyalkylbenzophenone. The methyl and propyl esters were prepared from 4-benzoylbenzoic acid by Fischer esterification. Esters of longer alkyl chains were made by refluxing the sodium salt of 4-benzoylbenzoic acid with about 0.9 equiv of the corresponding alkyl bromide in the minimum amount of *N*,*N*-dimethylformamide. A typical preparation is described below.

4-Benzoylbenzoic Acid Undecyl Ester. Sodium 4-benzoylbenzoate (3 g, 0.012 mol) and 1-bromoundecane (2.5 g, 0.0106 mol) were refluxed in 20 ml of *N*,*N*-dimethylformamide overnight. Completion of reaction was checked by TLC on silica gel (benzene). The product was extracted three times with 50 ml of hexane, washed twice with 25 ml of saturated sodium bicarbonate, and then washed with 30 ml of distilled water. After the solution was dried over anhydrous magnesium sulfate and the hexane removed, a pale yellow oil was obtained. It solidified upon standing, giving 2.54 g (~64% yield) of white product. It was chromatographed on a silica gel column using a mixture of 2% methylene chloride in benzene and then recrystallized twice from hexane. The melting point of the purified white crystal was 38.5-39 °C: NMR ($CDCl_3$, Me_4Si) δ: 1.1-2.0 (m, 18 H, aliphatic), 0.9 (t, J = 7 Hz, 3 H), 4.4 (t, J = 7 Hz, 2 H, CH_2O), 7.4-8.3 (m, 9 H, aromatic); ir (CCl_4): 1670 (ketone C=O), 1720 (ester C=O), 1100 cm^{-1}.

Esters **1** with alkyl chains longer than 11 carbons are solids at room temperature. They were prepared and purified similarly. Esters with the alkyl chain shorter than 11 carbons are pale yellow oils at room temperature (with the exception of the methyl ester which is a white solid). They were purified by vacuum distillation and column chromatography. Then they were recrystallized five times at low temperature.

All glassware used was cleaned by thorough rinsing with acetone and deionized water and then baked in the oven at 225 °C overnight. Cells for sample preparations in lifetime measurements were 10 cm × 1.3 cm Pyrex tubes equipped with a 19/38 female joint and a restriction inbetween to facilitate sealing after degassing. They were also equipped with grease traps. For the measurements of quantum yields of photoreaction, 1.000-cm quartz square cells, each fitted with a graded seal, a grease trap, a 19/38 female joint, and a 3-ml Pyrex reservoir for freezing in liquid nitrogen were used. All these cells were rinsed thoroughly with acetone and deionized water and dried.

An optical bench was used for the measurement of quantum yields. A 250-W medium-pressure mercury lamp (English Electric Co.) and a biconvex lens (fl 6 cm) were used to produce a parallel beam of light. Light in the 3660 Å region was isolated from the arc spectrum with (i) distilled water in a cylindrical Pyrex cell, (ii) an Oriel G-774-3550 filter, and (iii) a 366 nm interference filter.

A Xenon Corp. Nanopulser was used to produce single or repetitive flashes. It was aligned on an optical bench inside an aluminum box painted black. On the optical bench were appropriate lenses and filters, a sample holder with an outer jacket for temperature control, and a 1P28 photomultiplier tube. The details of the apparatus have been described previously.[22]

Lifetimes and Quantum Yields of Phosphorescence. All samples for lifetime measurements were prepared at concentrations of 5×10^{-4} to 2×10^{-3} M. They were degassed by five freeze-pump-thaw cycles at $<10^{-5}$ mm pressure. The same samples were used for the measurements of phosphorescence quantum yields. Emission spectra were obtained with a Hitachi Perkin-Elmer M2A fluorescence spectrophotometer at two wavelengths of excitation, λ_{ex} 325 and 345 nm. Emission intensities were compared with a standard sample of 5×10^{-3} benzophenone in carbon tetrachloride (τ = 106 μs) for which $\phi_p = 1.5 \times 10^{-2}$ has been reported.[24] Absorption corrections were applied for solutions of different concentrations: the uv spectrum of each sample (in the cylindrical tube) was run on a Cary 14 spectrophotometer. No blank cell was used; rather, the machine was zeroed at 410 nm. With careful alignment of the cells, Beer's law was obeyed. The corrections involved here were small. Values of ϕ_p were unaffected within experimental error (±10%) for excitation at 325 or 345 nm.

Intramolecular Photoreaction. Samples (10^{-3} M) were degassed by three freeze-pump-thaw cycles at better than 10^{-5} mm pressure. Photoreaction up to 20% was followed by observing the decrease in the absorbance of the benzophenone chromophore at 345 nm, using a Cary 16 spectrophotometer, at regular intervals (300 s) during the course of irradiation. The absorbances at 366 nm were also taken at the same time to enable correction for the change in the amount of light absorbed. Potassium ferrioxalate was used as a chemical actinometer. The data were treated by the method of Johns.[5]

Bimolecular Quenching Rate Constants. Bimolecular quenching rate constants with *n*-hexane, cyclohexane, 2-propanol, and naphthalene as quenchers were measured. In each measurement, a series of six samples containing varying amounts of quencher with the same amount of 4-carboxymethylbenzophenone (or benzophenone) were prepared and degassed. Quencher concentration was chosen in such a way that the lifetimes of the samples with quencher were reduced to within the range of 20–80% that of the sample free of the quencher. A measurement of τ as a function of quencher concentration enabled the computation of the rate constant. Data were fit by least squares to eq 3. Correlation coefficients were better than 0.98, and mean deviations in the slopes were less than 5% for individual runs. Since determination of a solvent effect on emission quenching by hexane was particularly important to aspects of this work, duplicate experiments were carried out.

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Photochemistry of Polyenes. IX. Excitation, Relaxation, and Deactivation of Dienes, Trienes, and Higher Polyenes in the Vitamin A Series in the Sensitized Isomerization Reaction[1]

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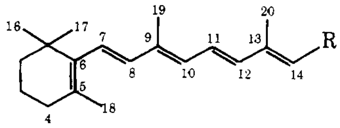
Abstract: In a detailed study of photosensitized isomerization of dienes, trienes, and higher polyenes in the vitamin A series it was found that dienes and trienes behave photochemically differently from the higher members of the series. Not only are the sterically hindered 7-cis isomers present in the photostationary states of the lower members but also under selective sensitization conversion to such isomers becomes quantitative, while for the longer polyenes 7-cis isomers are absent under all conditions of sensitized irradiation. This different photochemical behavior is explained in terms of the expected different structures of relaxed triplets, i.e., perpendicular ones in dienes and trienes and planar ones in higher polyenes. Direct irradiation was also reexamined with emphasis on the nature of the spin states where chemical reactions originate.

The problem of photochemical geometric isomerization of compounds in the vitamin A (Ia) series has, for many years, attracted the attention of many research groups. The system of retinal (Ib)[3] and related compounds[4] are still of intense current interest. Considering the important role of geometric isomerism in vision, the efforts are well justified.[5]



Ia, R = CH_2OH
b, R = CHO
c, R = CH_2OAc
d, R = CN

However, in spite of these efforts, the excited state properties of polyenes are still not well understood especially when compared to the wealth of information available for dienes and other smaller molecules. A major difficulty is to find a reliable analytical tool for systems where large numbers of isomers are expected. Therefore, when we started to investigate the photochemistry of vitamin A related compounds we decided to examine first the chemistry of the lower members of the series in some detail, where a lesser analytical problem is expected. It was hoped that the information so derived would facilitate the study of the chemistry of higher members. Also, it will be interesting to examine the differences, if any, in photochemical properties between polyenes of different length. We have, therefore, prepared the compounds II–IV and studied the photoisomerization reaction in some detail. Earlier we had also