Phosphorescence Emission Studies. The emission spectra were made on an Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. All emission spectra were recorded using a methanol–ethanol mixture (4:1) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. All compounds having relatively long radiative lifetimes were recorded on an *xy* plotter. Samples having short radiative lifetimes (<100 msec) were measured by photographing the decay curve on an oscillograph. The chopper was rotated manually to obtain the decay curve. The logarithmic intensities of the decay curve were plotted *vs.* time and the slope of the line at a logarithmic value of 2.303 gives the mean lifetime (τ).

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The Intra- and Intermolecular-Sensitized Photolysis of Substituted Benzoyl Peroxides

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Abstract: A series of substituted benzoyl peroxides has been prepared in which the substituent is a benzophenone-like sensitizer. In contrast to the related intermolecular system (benzoyl peroxide plus benzophenone), these peroxides photolyze with quantum yields approaching unity. The effectiveness of the sensitizer in various positions relative to the peroxide functional group has been studied by means of Stern–Volmer quenching experiments, emission experiments, and an intramolecular competition experiment with a diperoxide containing a central benzophenone moiety. Direct photolysis of benzoyl *m*-benzoylbenzoyl peroxide in CCl_4 gives chlorobenzene with enhanced proton magnetic resonance absorption; thermolysis gives chlorobenzene with enhanced emission. It is suggested that the low quantum yields obtained with benzoyl peroxide plus benzophenone are due to deactivation of an exciplex.

A salient characteristic of the benzophenone-sensitized photolysis of benzoyl peroxide is the low quantum yield. The work of Walling and Gibian[1] and of Smith[2] on the quantum yield at different peroxide concentrations has shown that the low yield is due to two factors: (i) an energy-transfer rate orders of magnitude below a diffusion-controlled value, and (ii) an inherently low efficiency of utilization of the energy even after the donor has been deactivated by the interaction with the peroxide molecule. In contrast, the quantum yields for the direct photolysis of dialkyl peroxides in the gas phase are near unity.[3,4] The quantum yield for the photolysis of dipropionyl peroxide in solution is moderately high, about 0.6.[5]

In the present paper we report some experiments with benzoyl peroxides having benzophenone-like chromophores as substituents.[6] The intramolecular transfer of excitation energy in these keto peroxides is fast and the utilization of the energy efficient, giving quantum yields near unity in most cases.

Although the intramolecular energy transfer is fast, the rate is still measurable by means of quenching experiments. The way in which the energy transfer depends on the intervening molecular structure suggests that the interaction between the ketonic n–π^* and peroxidic functional groups is largely of the "through-bonds"[7] variety rather than simply through space.

Other published work on the photolysis of diacyl peroxides has been concerned with the direct photolysis,[8] singlet-sensitized photolysis,[1,8f,9–14] and triplet-sensitized photolysis.[1,2,9,11,15] It has also been shown, by Kaptein, *et al.*,[11] and by Fahrenholtz and Trozzolo,[14] that the thermolysis and direct photolysis of ordinary diacyl peroxides produce singlet radical pairs while the sensitized photolysis gives either singlet or triplet pairs, depending on the sensitizer. A compound with a naphthyl-sensitizing substituent in the molecule, bis(3-(β-naphthyl)propanoyl) peroxide, has been studied by Kardash and Krongauz.[5]

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[3] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

[4] The absorption of dialkyl peroxides is continuous and the excited state appears to be dissociative.

[5] N. S. Kardash and V. A. Krongauz, *Teor. Eksp. Khim.*, **1**, 796 (1965).

[6] J. W. Miley, Ph.D. Dissertation, Florida State University, 1971.

[7] R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

[8] (a) O. J. Walker and G. L. E. Wild, *J. Chem. Soc.*, 1132 (1937); (b) J. K. Kochi and P. J. Krucic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969); (c) H. C. Box, E. E. Budzinski, and H. G. Freund, *ibid.*, **92**, 5305 (1970); (d) R. A. Sheldon and J. K. Kochi, *ibid.*, **92**, 4395 (1970); (e) J. C. Bevington and T. D. Lewis, *Trans. Faraday Soc.*, **54**, 1340 (1958); (f) N. N. Vasil'ev and V. A. Krongauz, *Kinet. Katal.*, **4**, 204 (1963).

[9] (a) F. G. Moses, Dissertation, California Institute of Technology, 1967. (b) The poor correlation between triplet energy and extent of decarboxylation found by Moses for the sensitized photolysis of acetyl peroxide may be due to the fact that some of the compounds included are actually singlet sensitizers. A case can be made for a separate correlation of the singlet energy and extent of decarboxylation.

[10] C. Luner and M. Szwarc, *J. Chem. Phys.*, **23**, 1978 (1955).

[11] R. Kaptein, J. A. den Hollander, D. Antheunis, and L. J. Oosterhoff, *Chem. Commun.*, 1687 (1970).

[12] V. A. Krongauz and I. N. Vasil'ev, *Kinet. Katal.*, **4**, 67 (1963).

[13] (a) T. Nakata, K. Tokumaru, and O. Simamura, *Tetrahedron Lett.*, 3303 (1967); (b) M. Kobayashi, H. Minato, and Y. Ogi, *Bull. Chem. Soc. Jap.*, **42**, 2737 (1969).

[14] S. R. Fahrenholtz and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **93**, 251 (1971).

[15] J. C. Martin and H. Hargis, private communication.

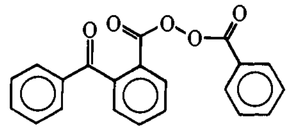
Table I. Products in CCl_4[a]

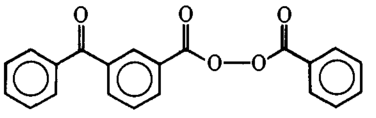
Peroxide	Initial concn, $M \times 10^2$	Yields, mol % of the peroxide: Chlorobenzene Th[b]	Chlorobenzene Ph[c]	Chlorobenzophenone Th[b]	Chlorobenzophenone Ph[c]	Cl_3CCCl_3 Th[b]	Cl_3CCCl_3 Ph[c]
p-BBP	1.42	94	99	96	96	84	84
m-BBP	2.32	82	89	89	91	73	78
	3.15	89	95	85	85	88	93
o-BBP	4.43	58	63	35[d]	42	45	68
	4.43[e]		76		54[e]		78
	2.32	60	83			41	90
Benzoyl	2.47	178[f]	184[f,g]			87[f]	74[f,g]
	2.47		164[f]				71[f]

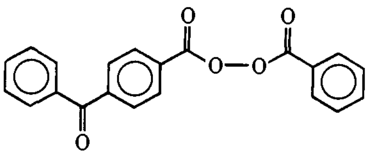
[a] Analyses by gas-liquid chromatography. [b] Thermolysis at 80°. [c] Photolysis with light from a Hanovia L697A 450-W medium-pressure mercury lamp, filtered by Corning glass filters 0-52 and 7-53, maximum intensity at 370 nm, half-height bandwidth 25 nm. [d] A trace of benzophenone and 13 mol % fluorenone were also found. [e] Heated to 80° for 24 hr after photolysis. Also contained a trace of benzophenone and 9 mol % fluorenone. [f] Benzoyl peroxide in the presence of 0.0426 M benzophenone. [g] Benzoyl peroxide heated at 80°for 24 hr after photolysis.

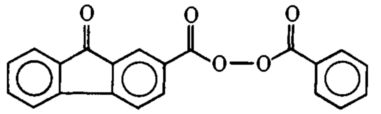
Results

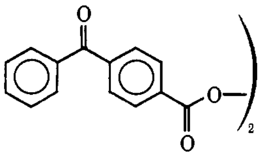
The Substituted Peroxides and Their Photolysis Products. The structures of the keto peroxides and our abbreviated names[16] for them are shown below.

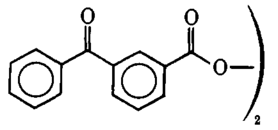

o-BBP

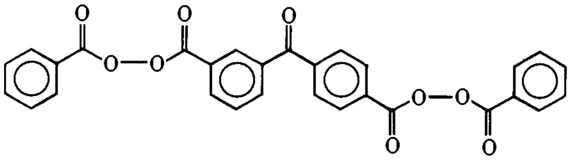

m-BBP

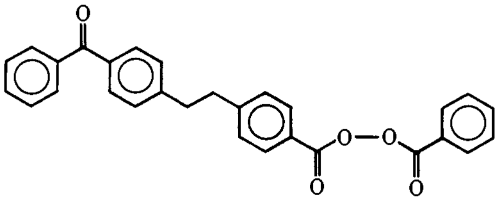

p-BBP


2-FP


p, p'-DBBP


m, m'-DBBP


m, p'-DP


p-BEP

From Table I it can be seen that the products from the photolysis of our peroxides in CCl_4, and using light on the long-wavelength side of the n–π* ketone carbonyl band, are largely the aryl chlorides to be expected from decarboxylation of the corresponding acyloxy radicals, followed by attack on the solvent. These are also the products of the thermal decomposition.

In the singlet-sensitized photolysis of benzoyl peroxide, there is produced about a 10% yield of a cage product, phenyl benzoate.[13] Neither phenyl benzoate nor the analogous products from the keto peroxides were formed in our experiments.

Quantum Yields. The quantum yield for the direct photolysis of *m*-BBP in CCl_4 at 30°, using less than 25% conversion to products, is 0.91 ± 0.07. This value is based on actinometry with benzophenone–benzhydrol[17] and with benzophenone–piperylene.[18] Ferrioxalate actinometry[19] gave an average quantum yield of 1.19, probably because the actinometer was not degassed. The quantum yield is independent of the initial concentration of the peroxide within the experimentally accessible range 0.03–0.10 M.

Because of their limited solubility in CCl_4, some of the other peroxides were studied in $CHCl_3$ and in benzene (Table II). In $CHCl_3$ the quantum yields for the peroxides with benzophenone part structures probably include some induced decomposition[20] since benzophenone triplets can form ketyl radicals in hydrogen-donating solvents. However, the quantum yield for *o*-BBP appears to be the same in $CHCl_3$ as in CCl_4. The

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(16) The *Chemical Abstract* names are: *o*-BBP, benzoyl *o*-benzoylbenzoyl peroxide; 2-FP, benzoyl (9-oxofluoren-2-yl)carbonyl peroxide; *m,m'*-DBBP, bis(*m*-benzoylbenzoyl) peroxide; *m,p'*-DP, benzoyl *m*-{*p*-[(benzoyldioxy)carbonyl]benzoyl} benzoyl peroxide; *p*-BEP, benzoyl *p*-(*p*-benzoylphenethyl)benzoyl peroxide.

(17) G. S. Hammond and R. P. Foss, *J. Phys. Chem.*, **68**, 3739 (1964).

(18) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(19) (a) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956); (b) J. Lee and H. H. Seliger, *J. Chem. Phys.*, **40**, 519 (1964).

(20) W. F. Smith, Jr., and B. W. Rossiter, *Tetrahedron*, **25**, 2059 (1969).

Table II. Quantum Yields

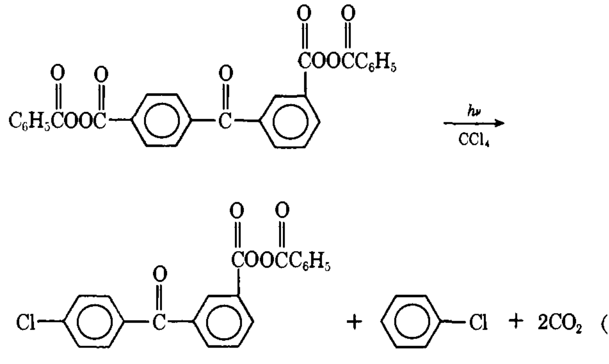
Peroxide	c_0, $M \times 10^2$	Solvent	% conversion	Actinometers[b]	Φ[a]
m-BBP	3–10	CCl_4	≤25	BB, BPip	0.91, 0.91
	4–6	$CHCl_3$	46–55	BB	1.29
	4–6	$CHCl_3$	42–55	*m*-BBP	1.10
	6	C_6H_6	14	*m*-BBP	0.76
o-BBP	6	CCl_4	29	BB, *m*-BBP	0.78, 0.72
	5	$CHCl_3$	28	*m*-BBP	0.70
p-BBP	6	$CHCl_3$	45	BB, *m*-BBP	1.24, 1.09
	6	$CHCl_3$	42	*m*-BBP	1.15
	5	C_6H_6	13	BPip, *m*-BBP	0.97, 0.86
m,p'-DP	5	$CHCl_3$	29	*m*-BBP	1.34
	3	C_6H_6	14	BPip, *m*-BBP	0.93, 0.82
2-FP	4	$CHCl_3$	40	*m*-BBP	0.81
p-BEP	4	$CHCl_3$	20	*m*-BBP	0.73
	4	$CHCl_3$	23	*m*-BBP	0.78
	4	C_6H_6	11	BPip, *m*-BBP	0.62, 0.57
m,m'-DBBP	6	C_6H_6	11	BPip, *m*-BBP	0.93, 0.83

[a] At 30°. [b] Actinometers: BB = benzophenone-benzhydrol redox; BPip = benzophenone-piperylene cis-trans isomerization; *m*-BBP = benzoyl *m*-benzoylbenzoyl peroxide in CCl_4, assuming Φ = 0.91.

quantum yields for benzoyl (9-oxofluoren-2-yl)carbonyl peroxide (2-FP) should be relatively free from induced decomposition components, since fluorenone does not readily photoreduce in alcohols or alkanes.[21,22] Intermolecular sensitization of benzoyl peroxide photolysis by fluorenone in benzene is reported not to occur at all.[1]

The quantum yields in benzene (Table II) are lower than those in CCl_4, perhaps because of quenching by unsaturated products. The lifetime of benzophenone triplet is also shorter in benzene.[23,24] The peroxide with an insulated chromophore (*p*-BEP) has a lower quantum yield (0.57) than the others, but this value is still significantly higher than the 0.25 fraction of decomposition reported by Walling and Gibian[1] for benzoyl peroxide "excited" by energy transfer from external benzophenone molecules.

The Diperoxide. The diperoxide *m,p'*-DP has about the same quantum yield as the monoperoxides. Only one peroxide functional group photolyzes per photon absorbed even though the energy supplied would be sufficient for two. Furthermore, there is about an 18:1 preferential photolysis of the *p*-peroxide group (eq 1).



(1)

Equation 1 was established as the principal process at low conversion (30% of the peroxide functional groups) by an experiment in which the remaining peroxide functions were reduced to carboxyl groups and converted to the corresponding methyl esters for analysis. The products and their yields are shown in Table III. The recovery of benzophenone moieties as diester (from unphotolyzed diperoxide), chlorocarbomethoxy benzophenones, and dichlorobenzophenone was 83%. The recovery of keto groups as dichlorobenzophenone was only 7%. This is about the amount of dichlorobenzophenone expected from the secondary photolysis of the monochloro peroxides. Photolysis of both peroxide functional groups of *m,p'*-DP in a single step is therefore negligible.

Table III. Photolysis of *m,p'*-DP[a]

Product	Mol %
Unphotolyzed peroxide, recovered as dimethyl ester	36
Half-photolyzed peroxide	
recovered as methyl *m*-(*p*-chlorobenzoyl)benzoate	38
recovered as methyl *p*-(*m*-chlorobenzoyl)benzoate	2
Completely photolyzed peroxide, as 3,4'-dichlorobenzophenone	7
Unphotolyzed benzoylperoxy groups, recovered as as methyl benzoate	141
Chlorobenzene	60
Hexachloroethane	58

[a] 0.00873 *M* in CCl_4 at 25°, carried to 30% of total peroxide functional groups photolyzed.

The ratio of benzoyl *m*-(*p*-chlorobenzoyl)benzoyl peroxide to benzoyl *p*-(*m*-chlorobenzoyl)benzoyl peroxide was obtained from an analysis of the mixture of the two methyl esters by means of the infrared spectrum. The mixture was found to consist of 95% 3-carbomethoxy-4'-chlorobenzophenone and only 5% 4-carbomethoxy-3'-chlorobenzophenone. This ratio of 19:1 should be lowered to 18:1 because about 15% of the chloroperoxides underwent secondary photolysis. The compound with the remaining peroxide function in the para position probably has a slightly greater extinction coefficient if the corresponding ester can be used as a model.

Quenching of the Excited Peroxides. Benzophenone and substituted benzophenones are usually considered to be triplet sensitizers, although it has recently been shown that there is an $S_0{}^1$ state only about 4 kcal/mol

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(21) W. E. Bachmann, *J. Amer. Chem. Soc.*, **55**, 391 (1933).
(22) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).
(23) J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *ibid.*, **92**, 410 (1970).
(24) W. D. K. Clark, A. D. Litt, and C. Steel, *ibid.*, **91**, 5413 (1969).

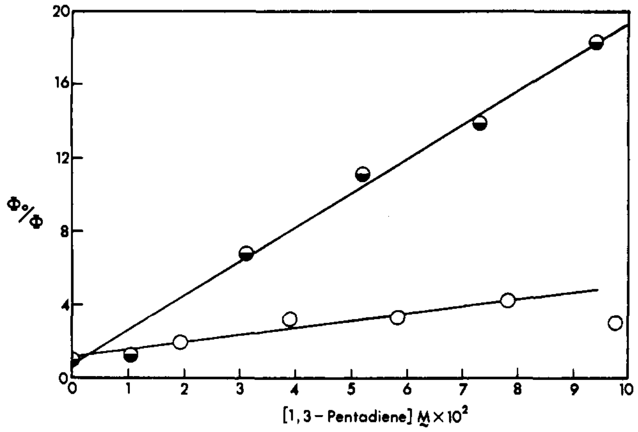

Figure. 1. Stern–Volmer plots for quenching by piperylene in CCl_4 of *m*-BBP (half-filled circles) and of *p*-BBP (empty circles).

above the $T_0{}^0$ state.[23] Piperylene quenches various benzophenone-sensitized reactions and undergoes cis–trans isomerization in the process, by energy transfer from the benzophenone triplet state rather than from the singlet.[18] This, of course, would indirectly quench any process involving the benzophenone $S_0{}^1$ singlet and can no longer be considered to be conclusive evidence for a triplet mechanism for the photoreaction being quenched. In any case, the photolysis of *m*-BBP and *p*-BBP in CCl_4 is quenched by piperylene, very efficiently in the case of the meta compound and somewhat less so in the case of the para compound. The Stern–Volmer plots are shown in Figure 1.

A pair of "triplet counting" experiments with benzophenone and with *m*-BBP in benzene showed that the peroxide causes the isomerization of exactly the same amount of the *trans*-piperylene as does benzophenone.

Values of $k_q\tau$ for the peroxidic benzophenone triplets, extracted from the quenching data using the Stern–Volmer expression (eq 2), are given in Table IV.

$$\frac{\phi_0}{\phi} = 1 + k_q\tau[Q] \qquad (2)$$

Table IV. Quenching in CCl_4 at 30°

Peroxide	$[P]_0$,[a] $M \times 10^2$	Quencher	$k_q\tau$, M^{-1}	τ,[c] sec × 10^9
m-BBP	3.4	*trans*-Piperylene	188	21
	6.6	Biacetyl	83[b]	10
	3.6	Anisole	1.3	
p-BBP	1.7	*trans*-Piperylene	40	4

[a] Initial peroxide concentration. [b] At room temperature, about 25°. [c] Calculated from $k_q\tau$ assuming diffusion-controlled quenching, η = 9.08 mP at 25°, 8.43 mP at 30°, and using the simplified Debye equation of ref 25

The rate constant k_q for the transfer of triplet energy to a quencher is believed to be equal to the encounter rate whenever transfer is exothermic by 3–4 kcal/mol.[25] Unfortunately, the actual encounter rate is probably less than, and only poorly approximated by, the value calculated from macroscopic diffusion constants.[26] Nevertheless, the value of τ obtained by dividing $k_q \times \tau$ by a calculated encounter rate constant is probably correct within an order of magnitude, and these are also collected in Table IV. The lifetime, τ, of our peroxidic benzophenones is presumably limited only by the decomposition of the peroxide functional group. The τ found for *p*-BBP is significantly less than that for *m*-BBP. Since the same quencher was used, any errors in the computed k_q should be the same. The decreased τ is consistent with the preferential decomposition of the *p*-peroxide functional group of *m,p'*-DP.

Our τ value of 21 × 10^{-9} sec is considerably shorter than the 10^{-4}-sec lifetime reported for benzophenone and benzophenone esters in CCl_4,[23] but not so short as the $<10^{-10}$-sec lifetime of benzophenones in which the energy can be transferred to a naphthalene or biphenyl substituent.[27]

Anisole, like benzene,[28] probably quenches benzophenones by a mechanism quite different from that of the other quenchers and the quenching rate is unlikely to be diffusion controlled.[29] If τ for *m*-BBP at 30° is still 21 × 10^{-9} sec, then the observed $k_q \times \tau$ value implies that k_q for quenching by anisole is about 6 × 10^7 M^{-1} sec^{-1}.

Intermolecular Sensitization. Because the previous work on the benzophenone–benzoyl peroxide system used benzene as solvent,[1,2] we repeated it using CCl_4 for comparison with our experiments on the intramolecular sensitization. The products (Table I) are analogous to those from the substituted peroxides. The quantum yields for benzoyl peroxide in CCl_4 (Table V) are about the same as in benzene at similar concentrations, so the differences between inter- and intramolecular sensitization are not very dependent on the solvent. The high quantum yield in $CHCl_3$ probably reflects the fact that ketyl radicals, formed reversibly in $CHCl_3$, can be intercepted by benzoyl peroxide.

Table V. Quantum Yields for Intermolecular Sensitization

Peroxide	Concn, $M \times 10^2$	Solvent	Sensitizer	Concn, $M \times 10^2$	% decomposed	Φ[a]
Benzoyl	3.64	CCl_4	Benzophenone	9.98	4.6	0.07
	5.68	CCl_4		4.66	3.1	0.18
	5.87	$CHCl_3$		4.66	9.4	0.58
m-BBP	1.96	CCl_4	*m*-Chlorobenzophenone	24.00	12.1	0.31[b]

[a] Based on *m*-BBP actinometry with $\phi_{\text{actinometer}}$ = 0 91. [b] Corrected from 0.35 because the peroxide absorbed 7% of the light.

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(25) A. A. Lamola, "Energy Transfer and Organic Photochemistry, Technique of Organic Chemistry," Vol. XIV, A. Weissberger, Ed., Interscience, New York, N. Y., 1969.

(26) C. A. Emeis and P. L. Fehder, *J. Amer. Chem. Soc.*, **92**, 2246 (1970).

(27) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, 87, 2322 (1965).

(28) J. Saltiel, H. C. Curtis, and B. Jones, *Mol. Photochem.*, 331 (1970).

(29) The singlet[30] and triplet[31] energies of anisole are 103 kcal mol^{-1} and 80 kcal mol^{-1}, well above the singlet and triplet energies of benzophenone. The mechanism[28,32] probably involves reversible addition of the benzophenone triplet to the aromatic ring. Hydrogen abstraction products were absent.

(30) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic, New York, N. Y., 1965.

(31) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Interscience, New York, N. Y., 1969.

(32) N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **91**, 7113 (1969).

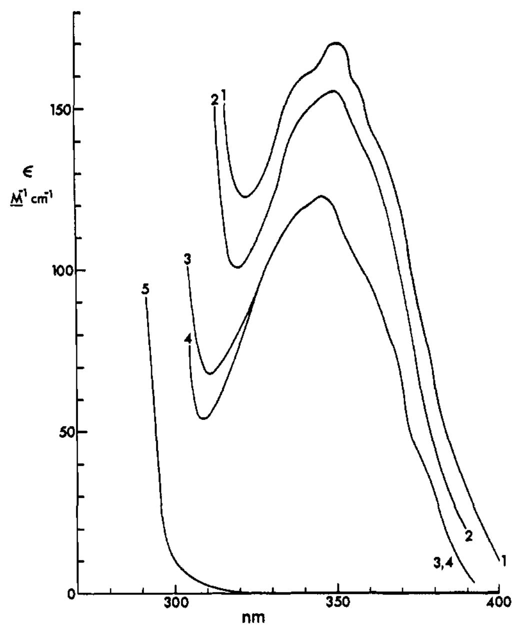

Figure 2. Absorption curves in CCl_4: curve 1, *m,p'*-DP or benzoyl *m*-{*p*-[(benzoyldioxy)carbonyl]benzoyl}benzoyl peroxide; curve 2, the related dimethyl ester, *m,p'*-dicarbomethoxybenzophenone; curve 3, benzoyl *m*-benzoylbenzoyl peroxide or *m*-BBP; curve 4, the related ester *m*-carbomethoxybenzophenone; curve 5, benzoyl peroxide.

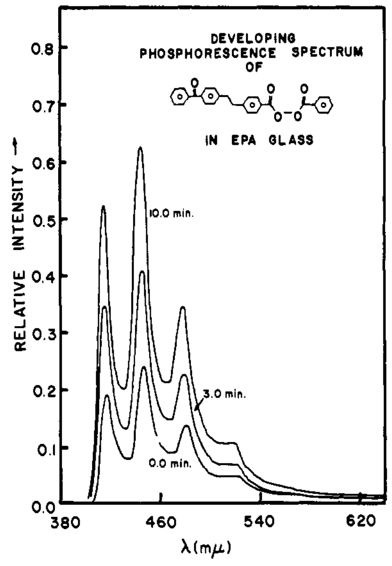

Figure 3. Developing phosphorescence spectrum from *p*-BEP in EPA glass.

The last line of Table V shows that the benzoyl substituent not only provides an intramolecular sensitization mechanism, *but also increases the quantum yield of the intermolecular process.* A similar result was obtained by Kardash and Krongauz[5] on introducing a naphthyl substituent into propionyl peroxide; the naphthyl substituent increased the quantum yield of the decomposition induced by energy transfer from external naphthyl chromophores above that found for propionyl peroxide plus naphthalene.

Chemically Induced Dynamic Nuclear Polarization (CIDNP).[11,14] The thermolysis of benzoyl *m*-benzoylbenzoyl peroxide (*m*-BBP) in CCl_3CH_2Cl at about 140° and in a field of about 1000 G gives chlorobenzene with an enhanced proton emission signal. Benzoyl peroxide behaves in the same way. Direct photolysis of *m*-BBP in CCl_4[33] at 25° in the 1000-G field gives an enhanced chlorobenzene absorption. That is to say, the direct (or internally sensitized) photolysis of *m*-BBP, like the benzophenone-sensitized photolysis of benzoyl peroxide in CCl_4,[11] gives triplet radical pairs.

Ultraviolet Absorption. The benzoyl-substituted peroxides behave like normal benzophenones with respect to absorption, with maxima in the range 330–350 nm and typical n–π* extinction coëfficients of 1–2 × 10^2 M^{-1} cm^{-1}.

The spectrum of benzoyl peroxide has a long tail that is detectable in concentrated solution (0.214 *M*) up to 390 nm and the other peroxides may have a similar weak tail overlapped by the much stronger n–π* transition. Simple peroxides have a similar, but still less intense continuously decreasing absorption in this region. For di-*tert*-butyl peroxide (gas) the extinction coefficient is only 0.9 at 305.1 nm and less than 0.1 at 340 nm.[3,34]

Emission. Irradiation of 3 × 10^{-3} *M* benzoyl *m*-benzoylbenzoyl peroxide (*m*-BBP) with 340-nm light in EPA glass at 77°K gives an emission spectrum resembling benzophenone phosphorescence,[23] but the intensity extrapolated to zero irradiation time is zero. The benzophenone-like phosphorescence is apparently due entirely to photolysis products, the triplet state of the peroxide itself being quenched before emission can occur. A similar experiment was carried out with the peroxide *p*-BEP, in which the peroxide and benzophenone structures are insulated by a saturated two-carbon bridge. With *p*-BEP there may be a significant initial emission (Figure 2), but the initial emission is still much weaker than the eventual emission of the photolysis products. Apparently the triplet state of this peroxide is also quenched, but not so completely as in the case of the conjugated *m*-BBP.[35]

Thermal Decomposition. The thermal decomposition of the substituted benzoyl peroxides was investigated briefly to ensure that there were no unusual effects of the substituents in the ground state.

Good first-order plots were obtained and there is no unusual amount of induced decomposition. The rate constants are also close to the values that would be predicted from the σ values of the substituents.[6,36]

The products of the thermolysis in CCl_4 are almost entirely hexachloroethane and the pair of aryl chlorides

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[33] Cl_3CCH_2Cl was used as the solvent in the thermal decomposition experiment for the sake of its high boiling point. CCl_4 was used in the photolysis of *m*-BBP at 25° because Cl_3CCH_2Cl failed to give enough C_6H_5Cl to detect in the nmr. Apparently the photolysis at low temperature in Cl_3CCH_2Cl gives benzoyloxy radicals that persist long enough to abstract hydrogen from the solvent. The light, from a medium pressure mercury lamp, was filtered through Pyrex.

(34) (a) D. H. Volman, *J. Chem. Phys.*, 17, 947 (1949); (b) D. H. Volman and W. M. Graven, *J. Amer. Chem. Soc.*, 75, 3111 (1953).

(35) Irradiation of benzoyl peroxide in EPA at 280 nm also gives zero initial emission and an emission after longer irradiation that is characteristic of a photoproduct. On thawing the glass, a yellow transient is observed. On refreezing and irradiating again there is a *different* initial emission spectrum, indicating further reaction of the photoproduct present in the glass before thawing. A yellow transient is also observed with benzoyl α-naphthoyl peroxide, but not with *m*-BBP. The yellow transients are apparently produced by the relaxation of still more reactive primary photoproducts trapped in the glass. Box, Budzinski, and Freund[8c] have observed pairs of trapped phenyl radicals in irradiated single crystals of benzoyl peroxide.

(36) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Amer. Chem. Soc.*, 72, 5426 (1950).

Table VI.[a] Some Simple Mechanisms Satisfying Equation 3

	Walling and Gibian	Mechanism II (additional steps)	Mechanism III (additional steps)
Reaction steps	$S + h\nu \xrightarrow{I_a\phi} S^*$ $S^* \xrightarrow{k_d} S$ $S^* + P \xrightarrow{k_t} P^* + S$ $P^* \xrightarrow{k_d'} P$ $P^* \xrightarrow{k_r}$ products	$S^* + P \xrightarrow{k_E} E$ $E \xrightarrow{k_d''} P + S$	$S^* + P \xrightarrow{k_E} E$ $E \xrightarrow{k_d''} P + S$ $E \xrightarrow{k_{rE}} P^* + S$ ($k_t = 0$)
Interpretation of $1/I$	$\frac{k_r}{k_r + k_d'}$, or efficiency of P*	$\frac{k_r}{k_r + k_d'} \times \frac{k_t}{k_t + k_E}$ product of two efficiencies	$\frac{k_{rE}}{k_{rE} + k_d''} \times \frac{k_r}{k_r + k_d'}$ product of two efficiencies
Interpretation of $\frac{I}{\lambda} \times k_d$	k_t	$k_t + k_E$	k_E

[a] S is sensitizer, P is peroxide, and E is an exciplex or excited-state complex.

corresponding to the peroxide (Table I). Except for those from *o*-BBP, better than 80% of the products are accounted for. Phenyl *p*-benzoylbenzoate, *p*-benzoylphenyl benzoate, and *p*-trichloromethylbenzoic acid were totally absent from the products of the thermolysis of the unsymmetrically substituted benzoyl peroxides, although analogous products are formed in small amounts in the decomposition of benzoyl peroxide.[37,38]

The products of the thermolysis of *m,m'*-DBBP and *p,p'*-DBBP in benzene[6] are the complicated mixture to be expected from the known behavior of benzoyl peroxide,[37] including benzoylbiphenyl, benzoylbenzoic acid, biphenyl, and benzophenone. The photolysis products were similar.[39]

Discussion

The keto peroxides photolyze with much higher quantum yields than are obtained in the photolysis of benzoyl peroxides sensitized with external benzophenone molecules. Walling and Gibian[1] have analyzed the low quantum yield for the benzoyl peroxide–benzophenone system in terms of two contributing factors, (i) a slow intermolecular energy transfer and (ii) a low efficiency for decomposition of the peroxide after it has accepted the energy. The energy-transfer rate constant and the efficiency were extracted from the slope λ and intercept I of a double reciprocal plot of quantum yield ϕ_{dec} and peroxide concentration $[p]$. Most of

$$\frac{1}{\phi_{\text{dec}}} = I + \lambda\frac{1}{[p]} \qquad (3)$$

the published data on various peroxide–sensitizer pairs fit an equation of the form of (3), which, however, can be predicted by more than one mechanism. The simplest is probably the one proposed by Walling and Gibian. Others are II and III of Table VI.

Energy Transfer Rate. For comparison of the intramolecular energy transfer rates of the keto peroxides with the intermolecular rates (k_t, $k_t + k_E$, or k_E; see Table VI) of peroxide plus external sensitizer, it is necessary to convert the second-order rate constants for the latter into equivalent first-order rate constants. The equivalent first-order process is energy transfer within a caged molecular pair of peroxide plus excited sensitizer. The excited pair is formed at a diffusion-controlled rate and then partitions by two first-order processes, one leading to excited peroxide plus sensitizer, the other to uncaged, solvent-separated peroxide plus excited sensitizer. If the latter is assumed to be a simple diffusion process complete when the molecules are separated by one molecular diameter (8 Å), it is possible to compute a first-order rate constant for the energy transfer within the caged pair from the observed k_t, M^{-1} sec^{-1} (or $k_t + k_E$ or k_E).[40] The first-order rate constant thus calculated is 3×10^6 sec^{-1} for energy transfer within the benzoyl peroxide–benzophenone caged pair, compared to 5×10^7 sec^{-1} for the intramolecular process in *m*-BBP and 2.5×10^8 sec^{-1} for *p*-BBP. Although all three of these numbers are approximate because of uncertainties in the theory of diffusion processes,[26] it is probably significant that they increase in ascending order from the nonbonded case to the meta bonded case to the para bonded case.[41]

The higher rate of energy transfer in *p*-BBP agrees with the outcome of the intramolecular competition experiment with the peroxide *m,p'*-DP in which one peroxide functional group is meta and the other para to the n–π^* carbonyl.

Finally, it should be noted that both the direct photolysis of *m*-BBP and the photolysis of benzoyl peroxide sensitized by benzophenone[11] give triplet radical pairs as shown by CIDNP experiments. If this were not the case it would be tempting to explain the less than

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[37] D. F. DeTar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *J. Amer. Chem. Soc.*, **89**, 4051 (1967).

[38] C. Walling and E. S. Savas, *ibid.*, **82**, 1739 (1960).

[39] The principal reason for our more extensive study of the *unsymmetrical* peroxides is their greater solubility in CCl$_4$, a solvent better suited to our purposes.

[40] We used the equations

$$k_D = \frac{6(D_A + D_B)}{s^2}$$

and

$$k_e = \frac{4\pi N_0(D_A + D_B)s}{1000}$$

for the rate constant k_D for diffusive separation by one molecular diameter s and for encounters, k_e.

[41] Molecular orbital calculations were carried out on a model system consisting of a diester analogous to the peroxide *m,p'*-DP. The n–π^* carbonyl group was simulated by adding an extra electron to the π system and increasing the electronegativity of the ketonic oxygen. Spin densities were found to be greater at the oxygen atoms of the para ester group than at the oxygens of the meta ester group. Frontier orbital coefficients were also found to be greater at the oxygen atoms of the para ester group.

Table VII. Properties of the Peroxides[e]

Peroxide	Dec point, °C	Anal., % Calcd C	Anal., % Calcd H	Anal., % Found C	Anal., % Found H	Infrared spectrum, cm^{-1}
Bis(*m*-benzoylbenzoyl) peroxide	124–125[a]	74.66	4.03 iodometric assay, 99%	74.72	4.10	
Bis(*p*-benzoylbenzoyl) peroxide	159–160	74.66	4.03 iodometric assay, 99%	74.21	4.07	
Benzoyl *m*-benzoylbenzoyl peroxide	99–99.5[b]	72.83	4.07 iodometric assay, ≥99%	73.03	4.02	Carbonyls at 1773, 1792, 1667
Benzoyl *p*-benzoylbenzoyl peroxide	144[c]	72.83	4.07 iodometric assay, 99.5%	72.49	4.07	
Benzoyl *o*-benzoylbenzoyl peroxide	97–98	72.83	4.07 iodometric assay, 99%	72.91	4.14	Carbonyls at 1785, 1760, 1667[d]
Benzoyl *m*-{*p*-[(benzoyldioxy)carbonyl]benzoyl}benzoyl peroxide	127 (detonates)	68.24	3.55 iodometric assay, 99%	68.08	3.62	
Benzoyl *p*-(*p*-benzoylphenethyl)benzoyl peroxide	137	77.32	4.92 iodometric assay, 98%	76.93	5.08	Carbonyls at 1786, 1767, 1658; strong aromatic peak at 1595
Benzoyl (9-oxofluoren-2-yl)carbonyl peroxide		73.25	3.51 iodometric assay, 98%	73.03	4.02	Bands at 1790, 1775, 1730, 1620

[a] Sample inserted at 122°, slow heating. [b] Sample inserted at 89°. [c] Inserted at 142°. Note that the melting point excludes the possibility of an equimolar mixture of the two symmetrical peroxides. [d] The spectrum excludes the alternative pseudo-structure. [e] Reference 6.

diffusion-controlled rate for the latter reaction in terms of an exclusively singlet mechanism. The small fraction of singlet n–π* benzophenone[23] would be about right to account for the lower rate.

Efficiency. For *m*-BBP, *p*-BBP, and *m,p*'-DP the quantum yields (see Table II) in inert solvents and in the absence of quencher are unity within experimental error. Hence the efficiency with which the peroxide functional group utilizes the energy, once delivered, must also be near unity. We suggest that the true efficiency of the decomposition of benzoyl peroxide, represented by $k_r/(k_r + k_d')$ in Table VI, is also high and that the low apparent efficiency (0.25–0.3) is due to deactivation of a triplet exciplex between peroxide and benzophenone. This would appear as a factor $k_t/(k_t + k_E)$ or $k_E/(k_{rE} + k_d'')$ as indicated in Table VI.

The quantum yields for *o*-BBP and the *p*-benzoylphenethyl-substituted compound *p*-BEP are also significantly lower than those for *m*- and *p*-BEP. We note that the ketonic C=O group of *p*-BEP is able to approach to within about 1.6 Å of the carbonyl oxygen of the benzoylperoxy group of that molecule. One of the conformations of *o*-BBP permits an even closer approach of the ketonic and benzoylperoxy carbonyl groups. Although slow energy transfer is plausible in the case of *p*-BEP, and has some support from the glass-phase luminescence experiments, we would expect energy transfer to be fast in the case of *o*-BBP just as it is in the case of *p*-BBP. The low yield of *o*-BBP might have the same cause (exciplex formation) as the low yield for benzoyl peroxide and benzophenone, but we suspect that it is due merely to quenching or internal filtering by the 9-fluorenone produced in the reaction.

A possible contributing cause of low efficiency in the photolysis of diacyl peroxides is cage recombination of acyloxy radical pairs. Judging from an isotopic scrambling experiment on the benzophenone-sensitized decomposition of benzoyl peroxide,[15] cage recombination is negligible, unless, of course, there is a significant proportion of recombination without scrambling. However, it does not seem at all plausible that *m*-BBP and *p*-BBP would give *less* cage recombination than benzoyl peroxide, and therefore we believe that cage recombination is not a major factor.

Intermolecular Energy Transfer to Keto-Substituted Peroxides. The enhanced quantum yield observed for *intermolecular* sensitization of *m*-BBP by chlorobenzophenone as compared to benzoyl peroxide sensitized by benzophenone (Table V) is probably due to the availability of an indirect path in which the energy is first transferred to the substituent chromophore and then intramolecularly to the peroxide functional group. Substituent effects on the triplet energy of benzophenone are very small,[23] and using the ester as a model we estimate that the E_T of the n–π* ketonic carbonyl of the peroxide is no more than 0.2 kcal/mol above that of the corresponding chlorobenzophenone. Although the energy transfer process may therefore require a slight activation it should still be quite fast.

Experimental Section

Quantum Yields and Actinometry. Quantum yield experiments were carried out in a "merry-go-round" apparatus.[42] A shutter was added to the instrument to permit turning and shaking the ampoules without turning off the lamp. Temperature was controlled by a thermostated water bath.

The light source was an Hanovia L679A 450-W medium-pressure mercury lamp immersed in a Pyrex cooling well. The 366-nm mercury line was isolated by means of Corning glass filters 0-52 and 7-73.[43] In a few instances product studies employed a Rayonet photochemical reactor using low-pressure mercury lamps RPR-2537A and RPR-3500A.[44] The RPR-2537A lamp emits 87% of its light at 253.7 nm and the RPR-3500 lamp emits 90% of its light between 310 and 410 nm.

Aliquots of the peroxide solution were degassed by three freeze-pump-thaw cycles, and duplicates or triplicates were run for each point.

Benzophenone-Benzhydrol Actinometry. The photoreduction of benzophenone was carried out as described by Hammond and Foss.[17] Five-milliliter aliquots of benzene solutions containing 0.1 *M* benzophenone and 0.02–0.20 *M* benzhydrol were degassed

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(42) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).

(43) R. P. Foss, D. O. Cowan, and G. S. Hammond, *J. Phys. Chem.*, 68, 3747 (1964).

(44) W. Lwowski and T. W. Mattingly, Jr., *J. Amer. Chem. Soc.*, 87, 1947 (1965).

in the usual manner. Sets of five different solutions were irradiated in parallel with the peroxide being studied. After irradiation, the contents of the ampoules were washed into 50-ml volumetric flasks, diluted with absolute methanol, and allowed to stand for 12–24 hr. The concentration of benzophenone before and after irradiation was then determined by measuring the uv absorption at 333 nm on a Beckman Model DU spectrophotometer. Originally the uv absorption was determined at several wavelengths as described by Hammond and Foss but this practice was abandoned when it was found that the average absorption was invariably very close to the reading at 333 nm. Apparently dilution with methanol instead of benzene solved whatever problem Hammond and Foss encountered.

Ferrioxalate Actinometry. The procedures of Hatchard and Parker[19a] and Calvert and Pitts[3] were used. The ferrioxalate concentration was set at 0.15 *M* to ensure that all light would be absorbed in the 16-mm tubes used. The best determination of the quantum yield for ferrous ion production upon irradiation of this concentration of potassium ferrioxalate with 366-nm light was made by Lee and Seliger who found Φ to be 1.20.[19b] An inert atmosphere was not used in the ferrioxalate actinometric experiments because of statements in the literature that it is not necessary.[3,19a] We found, however, that our ferrioxalate quantum yields were consistently higher than those obtained with the other actinometers.

Benzophenone–Piperylene Actinometry and Triplet Counting. A 4-ml aliquot of a 2 *M* stock solution of *trans*-piperylene in specially purified benzene[45] was added to 0.6 g of zone-refined benzophenone and diluted to 50 ml in a volumetric flask. For *m*-BBP triplet counting a 25-ml volumetric flask containing 0.4725 g of *m*-BBP was given a 2-ml aliquot of the stock piperylene. Five-milliliter aliquots of these solutions were degassed as usual, with liquid nitrogen as the coolant to prevent loss of piperylene. Glc analysis of the solutions before analysis showed that the solution contained 1.34% cyclopentene, 98.10% *trans*-piperylene, and 0.55% *cis*-piperylene. The concentration of piperylene corrected for cyclopentene was 0.1585 *M*. After irradiation both the benzophenone–piperylene solution and the *m*-BBP–piperylene solution were found to contain 2.52% cis based upon the area of the piperylene peaks.

Product Studies. The products from the thermal decomposition and photolyses of the peroxides were determined by conventional gas–liquid chromatographic methods.[6] The glc peaks were identified by collecting them on the plates of a Wilks Scientific Co. MIR-15 GC-IR multiple internal reflectance infrared cell.

For the internal competition experiment with *m,p'*-DP, that peroxide was irradiated until 30.4% of the original titer was lost. Chlorobenzene and hexachloroethane were determined in the usual way from one aliquot. The other products were determined from another aliquot after reduction of the remaining peroxides to the carboxylic acids with NaI in acetone. The acids were converted to their methyl esters by means of diazomethane; then the mixture was analyzed by glc for *m,p'*-dichlorobenzophenone, carbomethoxychlorobenzophenones, and *m,p'*-dicarbomethoxybenzophenone. Since the peak containing the *m*-carbomethoxy-*p'*-chlorobenzophenone and the *p*-carbomethoxy-*m'*-chlorobenzophenone could not be resolved, the mixture of these two esters was analyzed by means of its infrared spectrum, using the computer program ANALYZ.[46]

Synthesis of the Peroxides. Standard safety precautions included the use of all-glass equipment (including spatulas), explosion shields, and restriction of the experiments to a small scale. Of the new peroxides, only benzoyl *m*-{*p*-[(benzoyldioxy)carbonyl]benzoyl}benzoyl peroxide could be detonated with a hammer and it seemed to be less sensitive to shock than α-naphthoyl peroxide. The unsymmetrical peroxides were prepared by the technique of Greene and Kazan[47] from the corresponding acids, perbenzoic acid, and dicyclohexylcarbodiimide. Melting points, infrared spectra, and analyses of all of the peroxides are recorded in Table VII.

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[45] Benzene purified by selective photochemical chlorination of the hydrocarbon impurities was supplied by L. Metts and J. Saltiel.

[46] D. F. DeTar, *Anal. Chem.*, **38**, 1794 (1966).

[47] F. D. Greene and J. Kazan, *J. Org. Chem.*, **28**, 2168 (1963).

Crystal and Molecular Structure of the Photodimer of 5,6,7,8-Tetrahydro-2-quinolone

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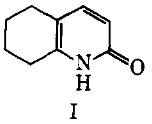
Abstract: The crystal and molecular structure of 1,3,4,7,8,9,10,11-octahydro-2*H*,5*H*-4a,11:10a,5-bis(iminomethano)dibenzo[*a,e*]cyclooctene-13,16-dione has been determined by a single-crystal X-ray diffraction study using diffractometer data. The compound crystallizes in the space group $P2_1/c$ with a = 9.892 (1) Å, b = 10.431 (1) Å, c = 7.272 (1) Å, β = 107.75 (1)°, Z = 2. The structure was determined by the symbolic addition method and refined by block-diagonal least squares to a final R value of 0.047 for the 1064 statistically significant, independent reflections. The C–C bond distance between monomer moieties, 1.623 (0.003) Å, is significantly longer than a normal C–C single bond and the amide system exhibits substantial conjugation.

Reactions involving the photolysis of 5,6,7,8-tetrahydro-2-quinolone (I) at 3500 Å yielded a highly labile and extremely insoluble compound. Its ir spectrum (Nujol) showed an unconjugated lactam absorption at 1660 cm^{-1}. Because of the extreme insolubility of the compound in the common organic solvents, no detailed ir, uv, or nmr spectra could be obtained. Mass spectral studies gave a molecular ion at *m/e* 149 which was identical with that obtained for I. Similarly, an nmr spectrum in trifluoroacetic acid was identical in every respect with that of the parent compound. The new compound must, therefore, be highly labile and readily revert to the starting material.[1]



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