Laser flash photolysis study of the photochemistry of ortho-benzoylbenzaldehyde

J.C. NETTO-FERREIRA

Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Itaguaí, Rio de Janeiro, Brazil, 23851

AND

J.C. SCAIANO

Department of Chemistry, University of Ottawa, Ottawa, Ont., Canada K1N 6N5

Received March 10, 1993

J.C. NETTO-FERREIRA and J.C. SCAIANO. Can. J. Chem. 71, 1209 (1993).

Ketene-enols **4** and **5** have been generated by laser flash photolysis of *ortho*-benzoylbenzaldehyde (**3**) and kinetically and spectroscopically characterized. In benzene or acetonitrile, the *E* ketene-enol, **4**, shows absorption at 340 and 400 nm and a lifetime in excess of 1 ms, whereas the *Z* ketene-enol, **5**, shows maxima at 360 and 430 nm and a lifetime of only 1.5 μ s. At shorter time scales we observed a weak absorption ($\lambda_{max} = 580$ nm) tentatively assigned to biradical **6** with a lifetime of 140 ns. The *E* ketene-enol is readily quenched by oxygen, dienophiles, methanol, and water, with quenching rate constants ranging from 3.6×10^3 M⁻¹ s⁻¹ (for methanol as a quencher) to 2.2×10^8 M⁻¹ s⁻¹ (for diethyl ketomalonate). At high water concentrations (typically >10 M) a new species, **7**, was detected showing maximum absorption at 510 nm and a growth lifetime of 7 μ s. In deuterated water and using the same concentration as before we observed a formation lifetime for **7** of 10 μ s, which results in an isotope effect of ~1.5. It is proposed that **5** is the main precursor for **7**. Steady-state irradiation of **3** in deaerated methanol leads to the formation of dihydroanthraquinone (**9**), a strongly colored and fluorescent ($\lambda_{max} = 475$ nm, $\tau_{fl} = 29$ ns) species, whereas 3-phenylphthalide (**2**, R = Ph) is the main product when the irradiation is performed in benzene. Steady-state quenching of product formation by diethyl ketomalonate gives a Stern–Volmer constant of 380 M⁻¹ from which we conclude that **5** is the ketene-enol responsible for product formation, in agreement with the laser flash photolysis results.

J.C. NETTO-FERREIRA et J.C. SCAIANO. Can. J. Chem. 71, 1209 (1993).

On a préparé les cétènes-énois 4 et 5 par photolyse flash au laser de l'ortho benzoyibenzaldéhyde (3) et on les a caractérisés cinétiquement et spectroscopiquement. Dans le benzène ou dans l'acétonitrile, le E cétène-énol, 4, absorbe à 340 et à 400 nm et a un temps de vie de >1 ms tandis que le Z cétène-énol, 5, montre des maxima à 360 et à 430 nm avec un temps de vie de 1,5 µs. Nous avons observé, dans des intervalles de temps plus courts, une faible absorption $(\lambda_{max} = 580 \text{ nm})$ que nous avons attribué au biradical 6, avec un temps de vie de 140 ns. Le *E* cétène-énol est facilement bloqué par l'oxygène, les diénophiles, le méthanol et l'eau avec des constantes de blocage allant de $3.6 \times 10^3 \,\mathrm{M^{-1}\,s^{-1}}$ (pour le méthanol comme agent de blocage) à 2.2×10^8 M⁻¹ s⁻¹ (pour le cétomalonate d'éthyle). Des concentrations élevées en eau (typiquement >10 M) permettent de déceler une nouvelle espèce présentant une absorption à 510 nm et un temps de croissance de 7 µs. Dans l'eau deutériée aux mêmes concentrations, on observe un temps de formation de 7 à 10 µs résultant d'un effet isotopique de 1,5 environ. On suggère que le composé 5 est le précurseur principal du composé 7. L'irradiation à l'état stationnaire du composé 3 dans le méthanol désaéré conduit à la formation de la dihydroanthraquinone (9), un composé fortement coloré et fluorescent ($\lambda_{max} = 475$ nm, $\tau_{II} = 20$ ns) tandis que le phthalide de phényl-3 (2, R = Ph) est le produit majoritaire lorsque l'irradiation a lieu dans le benzène. Le blocage à l'état stationnaire des produits obtenus à partir du cétomalonate d'éthyle donne une constante de Stern-Volmer de 380 M⁻¹ qui nous porte à conclure que le composé 5 est le cétène-énol responsable de la formation des produits en accord avec les résultats de la photolyse flash au laser.

[Traduit par la rédaction]

Introduction

Photoenolization of *ortho*-alkyl ketones is now a very well understood process. In most cases the transients involved in this intramolecular hydrogen abstraction reaction are well characterized as is the mechanism for the photoenolization process (1-20).

This is not the case for *ortho*-formyl aromatic aldehydes or ketones. Similarly to *ortho*-alkyl-substituted aromatic ketones, these compounds can form *ortho*-quinodimeththane-like structures by intramolecular hydrogen abstraction (reaction [1]). However, little is known about the transients involved in this process, especially for the case of *ortho*-acylbenzaldehydes.

From the photochemical point of view, *ortho*-phthaldehyde (1; R = H) is the most studied *ortho*-dicarbonyl compound (21–26). In this case, intramolecular hydrogen abstraction leads to the formation of a 1,4 biradical ($\tau =$ 1.6 μ s). Two triplet states, which are not responsible for product formation, are the precursors of this biradical, having lifetimes of 6 and 36 ns. Photolysis of *ortho*-phthalaldehyde leads to the formation of phthalide (**2**, **R** = H) and an isomeric mixture of dimeric products (21–25). Similar photochemical behavior has been observed for 2,3- and 3,4diformylpyridines (27), 2,3-diformylquinolines (27), and 2,3and 3,4-diformylthiophenes and selenophenes (28).



Recently, the ketene-enol probably involved in the decay

of the biradical from *ortho*-phthalaldehyde has been characterized by nitrogen matrix isolation studies (29).



The involvement of this kind of ketene-enol intermediate was also confirmed by low-temperature infrared studies on *ortho*-benzoylbenzaldehyde (3) (30). This compound is known to form 3-phenylphthalide (2, R = Ph) in an almost quantitative yield upon irradiation at low temperature (reaction [2]) (31).



The reactions of ketenes have been the subject of a recent review (32), and their reaction with water has been the subject of theoretical studies (33, 34).

In this paper we report an extensive study of the photochemistry of 3 in which we identify and characterize the transients involved in the phototransformation of reaction [2]. Our approach involves a combination of laser flash photolysis, steady-state irradiation, and emission and absorption spectroscopy.

Experimental part

Materials

The solvents benzene (Aldrich), acetonitrile (Fisher), and methanol (Aldrich) were used as received and were all Spectrograde.

Maleic anhydride (Aldrich), diethyl ketomalonate (Aldrich), dimethyl acetylenedicarboxylate (Aldrich), water (Omni, HPLC grade), and deuterated water (MSD isotopes) were used as received.

ortho-Benzoylbenzaldehyde was synthesized from the methyl ester of ortho-benzoylbenzoic acid using a literature procedure (35, 36). Its physical and spectroscopic properties agree well with the values found in the literature and are in accord with the proposed structure: mp 66–67°C (lit. (36) mp 64–67°C); ¹H NMR (CDCl₃) δ (ppm): 9.98 (s, 1H), 7.75 (m, 9H); MS m/z (%): 210 (100, M⁺), 181(94), 105(28), 77(39).

General techniques

UV–VIS spectra were recorded with a HP-8451A diode array spectrometer. Phosphorescence and fluoroescence spectra were recorded with a Perkin Elmer LS-50 spectrofluorimeter.

GC analyses were carried out on a Perkin Elmer model 8320 capillary gas chromatograph employing a 12-m J&W bonded-phase vitreous BP1 silicone column. GC–MS analyses were performed in a Hewlett–Packard model 5995 system using a similar column.

Melting points were determined in a Mel-Temp apparatus and were not corrected.

The ¹H NMR spectrum was recorded on a Varian 200 MHz spectrometer model Gemini-200, using CDCl₃ as a solvent.

Product studies and quantum yield determinations

Typical samples were 1.0 mL containing 0.02 M ketone in benzene or methanol and were deaerated by bubbling with oxygen-free nitrogen. The samples were contained in Pyrex tubes and irradiated in a merry-go-round with nine RPR-3000 Å lamps. The products were characterized by GC-MS. Dodecane was used as internal standard in the steady-state quenching experiments.

For the quantum yield determinations the photofragmentation of valerophenone in benzene was employed as actinometer, taking the quantum yield of acetophenone formation as 0.30 (37).

Laser flash photolysis

Samples were contained in cells constructed of 7 mm \times 7 mm Suprasil tubing and were deaerated by bubbling oxygen-free nitrogen. The samples were irradiated with the pulses (308 nm, ~5 ns, \leq 25 mJ/pulse) from a Lumonics model 510 excimer laser operated with Xe–HCl–He mixtures. The signals from an RCA-4840 photomultiplier were initially captured by a Tektronix 2440 transient digitizer and then transferred to a Macintosh IIci computer that controlled the experiment and provided suitable storage, processing, and hard-copy capabilities. This system operated under LabVIEW-2.2 software and will be described in detail elsewhere. The system is otherwise similar to that employed in earlier work (38, 39).

Results

Phosphorescence spectroscopy

The phosphorescence spectrum for ketone **3** in an EPA (diethylether: isopentane: ethanol) glass at 77 K shows vibrational structure characteristic of a n,π^* triplet ketone. From the 0,0 emission band in this spectrum we obtain a triplet energy of 69.5 kcal/mol, which is very close to the value of 69 kcal/mol for benzophenone (40, 41). Clearly the emitting chromophore is localized on the benzophenone moiety. The small difference may reflect out-of-plane twisting of the *o*-formyl phenyl system.

Laser flash photolysis studies

(a) Transient characterization

Irradiation of a 3.0 mM solution of **3** in benzene or acetonitrile with the 308-nm pulses from an excimer laser leads to the formation of a readily detectable transient that shows absorptions at 340 and 400 nm (Fig. 1*a*). The decay monitored at either of these two maxima shows short- and longlived transients; the latter has a lifetime in excess of 1 ms. It was not quenched by the usual triplet quenchers such as dienes and was only moderately quenched by oxygen. To this species we assign the structure **4**, corresponding to the *E* ketene-enol, consistent with the intramolecular hydrogen transfer mechanism usually observed in the case of photoenolizable ketones (vide infra) (3, 16).



On shorter time scales, the spectrum recorded 0.5 μ s after laser excitation is considerably different from that recorded at a delay of 5 μ s (Fig. 1*b*). In the former case the decay shows contributions from a short- and a long-lived transient (Fig. 2). Subtracting the spectrum at 5 μ s delay, i.e., that due to 4, from the early spectrum corresponding to the sum of the short- and long-lived transients, we obtain maxima at 360 and 430 nm for the short-lived species (Fig. 3). To this intermediate, having a lifetime of 1.5 μ s, we assign structure 5, corresponding to the Z ketene-enol. This is the first example where the Z and E enols show significant spectral differences.



Fig 1. (a) Transient absorption spectrum obtained on 308-nm excitation of 3.0 mM *ortho*-benzoylbenzaldehyde (3) in benzene and recorded 0.5 μ s after the laser pulse. (b) Same as above but recorded 5 μ s after the laser pulse.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by SAVANNAHRIVNATLABBF on 11/12/14 For personal use only.



FIG. 2. Decay trace monitored at 365 nm due to the transient generated by excitation of 3.0 mM ortho-benzoylbenzaldehyde (3) in benzene.





FIG. 3. Difference spectrum from the subtraction of spectrum in Fig. 1b from the one in Fig. 1a and attributed to the Z keteneenol.

In benzene, at 320 nm, we observe the formation of a new species, that grows-in with first-order kinetics and a lifetime of 1.5 μ s at room temperature. Since 2 (R = Ph) has a strong absorption at this wavelength we can attribute this signal to product formation. The fact that 5 is decaying with the same lifetime as 2 is growing-in indicates that the former species is the precursor of the latter (2, R = Ph).

The biradical 6, precursor of the ketene-enols 4 and 5, has a very weak absorption (only 0.005 absorbance units) at 580 nm, as previously indicated (31), with a lifetime of 140 ns. This species is quenched by oxygen ($k_q = 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) in benzene, but not by 1,3-cyclohexadiene, a typical triplet quencher, which is fully consistent with its assignment as the 1,4-biradical. We note that, just as in other systems involving photoenolization, this biradical can also be viewed as the triplet state of the ketene-enol.



Attempts to detect the triplet state of **3** were (not surprisingly) unsuccessful. Addition of 1,3-cyclohexadiene in concentrations of 0.025 M had virtually no effect ($\leq 10\%$) on the yield of ketene in benzene. Thus, if the precursor of the ketene is the triplet ketone one must conclude that its lifetime is less than 2 ns. Naturally, an alternative explanation would be that the reaction leading to the ketene does not take place from the triplet manifold; given the phosphorescence spectrum of **3** (vide supra) and the fact that benzophenones normally undergo intersystem crossing with unit efficiency this explanation appears unlikely.

(b) Intermolecular reactivity

The *E* ketene-enol **4** can be quenched by dienophiles, methanol, water, and oxygen. For example, oxygen quenching is rather sluggish with $k_q = 2.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$; reaction of photoenols with oxygen has been reported before (42, 43). For diethyl ketomalonate we measured a quenching rate constant of $2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Dimethyl



FIG. 4. Absorption spectrum obtained on 308-nm excitation of *ortho*-benzoylbenzaldehyde (3) in acetonitrile:water (4:1). Insert: Growth recorded at 500 nm due to 7, generated as above.

TABLE 1.	Quenching	rate	constants	for	the	Ε	ketene-enol	4	de-
		I	rived from	3 ^a					

	$k_{q}(M^{-1} s^{-1})$					
Quencher	4	8 ^b				
Oxygen	2.5×10^{6}					
Maleic anhydride	4.1×10^{6}	1.4×10^{4}				
Diethyl ketomalonate	2.2×10^{8}	7.8×10^{5}				
Dimethyl acetylenedicarboxylate	$< 10^{3}$					
Methanol	3.6×10^{3}	7.9×10^{3}				
Water	1.1×10^{3}					

"In acetonitrile.

"From Ref. 48.

acetylenedicarboxylate in concentrations up to 0.08 M did not have any effect on the lifetime of the *E* ketene-enol.

In neat methanol (ca. 25 M) the lifetime for **4** is greatly decreased ($\tau = 12 \ \mu s$). A plot of the rate constant for ketene decay as a function of methanol concentration in the 0–6 M range led to a linear plot and a quenching rate constant of $\sim 3 \times 10^3 \ M^{-1} \ s^{-1}$. Interestingly, extrapolation to neat methanol yields almost exactly the observed lifetime of 12 μs .

Quenching by water follows a linear dependence with water concentration (0–12 M range examined) and is remarkable since, besides the considerable shortening of the lifetime for 4, one can observe the formation of a new species. The formation of this new intermediate is most readily observed when the water concentration exceeds 10 M. The broad absorption centered at 510 nm (Fig. 4) grows-in with first-order kinetics and a lifetime of 7 μ s for its formation (see insert in Fig. 4). That this quenching process involves some form of hydrogen transfer can be shown by using deuterated water as a quencher. In this case the species absorbing at 510 nm grows-in with a lifetime of 10 μ s, resulting in a deuterium isotope effect of ~1.5 (44). To this species we assign structure 7, corresponding to the ketene-hydrate,

formed by a nucleophilic attack of water on the ketene. It should be noted that the formation of 7 is much faster than the decay of 4, by at least an order of magnitude. We were initially puzzled by this observation; however, we believe that 7 results from water addition to 5, rather than 4. While the extensive spectral overlap in the presence of water makes it difficult to carry out accurate kinetic measurements on 5, the traces at 430 nm reveal quite clearly that 5 is decaying in the same time scale in which 7 is formed. From the growth kinetics for 7, one can estimate a rate of reaction of 5 with water of $\sim 1.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Of course, the ketene-hydrate (or carboxylic acid enol) is expected to form the carboxylic acid (in a process too slow for our detection system) and ultimately to form the same lactone as reaction [2]. This mechanism is similar to that proposed for the reaction of arylketenes with alcohols (45). Other ketene hydrates have recently been reported (46, 47). Quenching of the ketene-enol by water in methanol solvent was slightly faster than in acetonitrile $(k_q > \sim 1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1})$.



Table 1 shows quenching rate constants for several quenchers. These values are comparable to those reported for the quenching of the vinylketene 8 (10, 48).



Product studies and quantum yield determinations Irradiation of deaerated samples containing 3 in benzene leads to the formation of 3-phenylphthalide (2, R = Ph) as

the main product (see Scheme 1), together with a small amount of anthraquinone. In methanol, which as already pointed out is a good quencher for the E ketene-enol (4), we observed the development of an intense yellow color in the solution after a few minutes of irradiation. In fact, this colored species is so long-lived in the absence of oxygen that under continuous irradiation its formation could be monitored in a conventional UV-visible spectrophotometer (Fig. 5). This new species is strongly fluorescent, showing emission with λ_{max} 475 nm, and a fluorescence lifetime of 29 ns. Oxygen bubbling causes an almost complete disappearance of the yellow color and eliminates the fluorescence emission. Surprisingly, GC analysis of the irradiation product from 3 in methanol did not show the formation of any new product, although the amount of anthraquinone formed in this case is considerably higher than in benzene. Interestingly no evidence was found for the formation of 11, a possible product from the rearrangement of 10.



This observation can be explained by assuming that in methanol the formation of dihydroanthraquinone (9), a highly colored and fluorescent species (10, 11, 49–51), is probably favored by an increase in the electrophilicity of the carbon atom responsible for the cyclization reaction. The overall process is shown in Scheme 1.



Quantum yield determinations were carried out using the formation of acetophenone from valerophenone as a relative actinometer ($\Phi = 0.30$) (37). In benzene we measured a value of 0.18 ± 0.02 for the quantum yield of formation of 3-phenylphthalide (**2**, R = Ph) under nitrogen.

Steady state quenching

As proposed before, the irradiation of ortho-benzoylbenzaldehyde (3) can lead to the formation of two isomeric ketene-enols, 4 and 5, and inspection of their structures and transient behavior leads us to assume that product formation must come from the short-lived species, the Z isomer 5. To confirm this reasoning we decided to use the fact that diethyl ketomalonate is an excellent quencher for the E ketene-enol 4 (vide supra), and tried to quench product formation under steady-state irradiation conditions. To carry out these measurements, several samples, each containing 1 mL of a stock solution of 3 in benzene and different concentrations for the quencher, were irradiated in a merrygo-round inside a Rayonet photoreactor equipped with nine RPR-3000 Å lamps. Figure 6 shows a plot of relative quantum yield against diethyl ketomalonate from which one can obtain $K_{\rm SV} = 380 \, {\rm M}^{-1}$. Assuming the reactive species is 5, and taking into account its lifetime, leads to a rate constant for quenching of $2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, a value remarkably similar to that measured directly for $4 (2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$. In contrast, if one were to assume the reactive species to be 4, then, given the known lifetime (>1 ms) and experimentally measured rate constant, one would have predicted a Stern–Volmer slope of $\ge 2 \times 10^5 \text{ M}^{-1}$, in sharp disagreement with the experimental value of 380 M⁻¹. Thus, comparison of transient and quantum yield data identify 5 as the reactive species leading to product formation.

Discussion

The excited triplet state of *ortho*-benzoylbenzaldehyde, 3, shows typical benzophenone-like characteristics. Compound 3 can be viewed as having two chromophores, resembling benzophenone and benzaldehyde. The triplet state from the latter is expected to be located at higher energy ($\sim 4-5$ kcal/mol higher) than the benzophenone triplet.

Photolysis of **3** involves the expected photoenolization, a process that has been well characterized in many other aromatic ketones with labile hydrogens in the *ortho* position (3, 16). The case of **3** is rather special since the transient products are the ketene-enols **4** and **5**. We assume that the precursor to these enols is the triplet state of **3**; while this species has not been detected, its lifetime would be expected to be very short. The observation is in line with those for other photoenolizable benzophenones (10-12, 50, 52).

Interestingly, 4 and 5 show significant differences in their absorption spectra, as illustrated in Figs. 1b and 3. MM2 calculations suggest that the enol moiety can approach planarity most easily in the case of 5; increased conjugation presumably leads to the red shift in the case of the short-lived 5.

Two results are rather surprising: (a) that reaction of the ketene with water and alcohols would follow first-order kinetics and (b) that formation of 7 would involve either 5 (the Z ketene-enol) exclusively, or at least that formation from Zthis precursor would be much faster and more efficient than from 4.² There are clear examples in the literature where water addition has been demonstrated to frequently (but not always) (44) require two molecules of water (47, 53, 54) and theoretical work provides an interpretation for this observation (33, 34). If we think of these two water molecules as one for adding and the second one as "assisting" the addition, we can conceive that in the case of 5 the hydroxylic group already present can provide this assistance in an intramolecular fashion. Naturally, in the case of 4 the -OH group is not suitably oriented to assist water addition or at least not to do this with comparable efficiency. In addition, the fact that 5 is more planar than 4 may facilitate the nucleophilic attachment by water by delocalizing more easily the negative charge generated, in a manner similar to that proposed for phenylketene (55).

The isotope effect observed in the hydration reaction $(H/D \sim 1.5)$ is in line with those observed by other groups for other ketene reactions with water, which values frequently fluctuate between 1.5 and 2.5 (44, 54–57).

Acknowledgements

Some of the early experiments in this work were carried out at the National Research Council laboratories in Ottawa,

 $^{^{2}}$ We cannot exclude some slow underlying formation of 7 from 4.









FIG. 6. Quenching plot of relative quantum yield for phthalide (2, R = Ph) formation from 3 vs. [diethyl ketomalonate].

Canada; the support received during that stage of the work is gratefully acknowledged. Thanks are due to Mr. D. Lindsay (NRC, Ottawa) for carrying out the GC–MS measurements. This research has been supported by an operating grant (J.C.S.) from the Natural Sciences and Engineering Research Council of Canada.

- 1. N.C. Yang and C. Rivas. J. Am. Chem. Soc. 83, 2213 (1961).
- E.F. Zwicker, L.I. Grossweiner, and N.C. Yang. J. Am. Chem. Soc. 85, 2671 (1963).
- 3. P.G. Sammes. Tetrahedron, 32, 405 (1976).
- 4. R. Haag, J. Wirz, and P.J. Wagner. Helv. Chim. Acta, 60, 2595 (1977).
- P.K. Das, M.V. Encinas, R.D. Small, Jr., and J.C. Scaiano. J. Am. Chem. Soc. 101, 6965 (1979).
- 6. J.C. Scaiano. Chem. Phys. Lett. 73, 319 (1980).
- 7. K.H. Grellmann, H. Weller, and E. Tauer. Chem. Phys. Lett. **95**, 195 (1983).
- A. Beckett and G. Porter. Trans. Faraday Soc. 59, 2051 (1963).
- 9. E.F. Ullman and K.R. Huffman. Tetrahedron Lett. 1863 (1965).
- 10. G. Porter and M.F. Tchir. Chem. Commun. 1372 (1970).
- 11. G. Porter and M.F. Tchir. J. Chem. Soc. A, 3772 (1971).
- 12. P.K. Das and J.C. Scaiano. J. Photochem. 12, 85 (1980).
- 13. K. Uji-le, K. Kikuchi, and H. Kokubun. J. Photochem. 10, 145 (1979).
- P.J. Wagner and C.-P. Chen. J. Am. Chem. Soc. 98, 239 (1976).
- N.D. Heindel, E.W. Sarver, and M.A. Pfau. Tetrahedron Lett. 3579 (1968).
- 16. P.J. Wagner. Pure Appl. Chem. 49, 259 (1977).
- 17. B. Guérin and L.J. Johnston. Can. J. Chem. 67, 473 (1989).
- J.C. Netto-Ferreira and J.C. Scaiano. J. Am. Chem. Soc. 113, 5800 (1991).
- M. Pfau, S. Combrisson, J.E. Rowe, Jr., and N.D. Heindel. Tetrahedron, 34, 3459 (1978).
- 20. P.J. Wagner, D. Subrahmanyam, and B.S. Park. J. Am. Chem. Soc. **113**, 709 (1991).
- 21. A. Schönberg and A. Mustafa. J. Am. Chem. Soc. 77, 5755 (1955).
- 22. J. Kagan. Tetrahedron Lett. 6097 (1966).
- 23. S.P. Pappas and J.E. Blackwell, Jr. Tetrahedron Lett. 3337 (1968).
- 24. K.F. Cohen, J.T. Pinhey, and R.J. Smith. Tetrahedron Lett. 4729 (1968).
- D.A. Harrison, R.N. Schwartz, and J. Kagan. J. Am. Chem. Soc. 92, 5793 (1970).
- J.C. Scaiano, M.V. Encinas, and M.V. George. J. Chem. Soc. Perkin Trans. 2, 724 (1980).
- G. Quequiner and A. Godard. C. R. Seances Acad. Sci. Ser. C.: 269, 1648 (1969).
- C. Paulmier, J. Bourguinon, J. Morel, and P. Pastour. C. R. Seances Acad. Sci. Ser. C: 270, 494 (1970).

- 29. J. Gebicki and S. Kuberski. J. Chem. Soc. Chem. Commun. 1364 (1988).
- 30. M. Tada and T. Maeda. Chem. Ind. (London), 742 (1976).
- M. Pfau, J. Molnar, and N.D. Heindel. Bull. Chim. Soc. Fr. 34, 164 (1983).
- 32. T.T. Tidwell. Acc. Chem. Res. 23, 273 (1990).
- M.T. Nguyen and A.F. Hegarty. J. Am. Chem. Soc. 106, 1552 (1984).
- J. Andraos, A.J. Kresge, M.R. Peterson, and I.G. Csizmadia. J. Mol. Struct. (Theochem), 232, 155 (1991).
- 35. W.A. Bonner. J. Am. Chem. Soc. 85, 439 (1963).
- M. Metlesics, T. Anton, M. Chaykovsky, V. Toome, and L.H. Sternbach. J. Org. Chem. 33, 2874 (1968).
- P.J. Wagner, P.A. Kelso, A.E. Kemppainen, J.M. McGrath, H.N. Schott, and R.G. Zepp. J. Am. Chem. Soc. 94, 7506 (1972).
- 38. J.C. Scaiano. J. Am. Chem. Soc. 102, 7747 (1980).
- 39. J.C. Scaiano, M. Tanner, and D. Weir. J. Am. Chem. Soc. 107, 4396 (1985).
- S.L. Murov. Handbook of photochemistry. Marcel Dekker, New York. 1973.
- 41. I. Carmichael and G.L. Hug. Spectroscopy and intramolecular photophysics of triplet states. *In* Handbook of organic photochemistry. *Edited by* J.C. Sciano. CRC Press, Boca Raton, Fla. 1989. p. 369.
- 42. M. Pfau, E.W. Sarver, and N.D. Heindel. C.R. Acad. Sci. 1167 (1969).
- 43. M. Juliard and M. Pfau. J. Chem. Soc. 184 (1976).
- 44. E. Bothe, A.M. Dessouki, and D. Schulte-Frohlinde. J. Phys. Chem. 84, 3270 (1980).
- 45. J. Jähme and C. Rüchard. Tetrahedron Lett. 23, 4011 (1982).
- B. Urwyler and J. Wirz. Angew. Chem. Int. Ed. Engl. 29, 790 (1990).
- M. Barra, T.A. Fisher, G.J. Cernigliaro, R. Sinta, and J.C. Scaiano. J. Am. Chem. Soc. 114, 2630 (1992).
- P. Schiess, M. Eberle, M. Huys-Francotte, and J. Wirz. Tetrahedron Lett. 25, 2201 (1984).
- 49. P.G. Sammes and T.W. Wallace. J. Chem. Soc. Perkin Trans. 1, 1845 (1975).
- N.D. Heindel, J. Molnar, and M. Pfau. J. Chem. Soc. Chem. Commun. 1373 (1970).
- W.A. Henderson, Jr. and E.F. Ullman. J. Am. Chem. Soc. 87, 5424 (1965).
- K. Uji-ie, K. Kikuchi, and H. Kokubun. Chem. Lett. 5, 499 (1977).
- 53. P.J. Lillford and D.P.N. Satchell. J. Chem. Soc. B, 889 (1968).
- 54. D.P.N. Satchell and R.S. Satchell. Chem. Soc. Rev. 4, 231 (1975).
- 55. A.D. Allen, A.J. Kresge, N.P. Schepp, and T.T. Tidwell. Can. J. Chem. **65**, 1719 (1987).
- 56. E. Bothe, H. Meier, D. Schulte-Frohlinde, and C. von Sonntag. Angew. Chem. Int. Ed. Engl. 15, 380 (1976).
- 57. S.H. Kabir, H.R. Saikaly, and T.T. Tidwell. J. Am. Chem. Soc. **101**, 1059 (1979).