Thus the frontier orbitals of both compounds are derived from the perimeter orbitals, but in **1** the unperturbed nonbonding perimeter orbital is the LUMO and in **2** it is the HOMO. As an immediate consequence, **1** is easily reduced and **2** is easily oxidized.

Although the HOMO-LUMO splittings in **1** and **2** are comparable in magnitude, the changes in the electronic structure arising from the perturbation are basically different in nature. In the case of **2**, the HOMO is nonbonding between *all* adjacent C atoms of the periphery, and hence, the perturbation does not favor bond-length alternation. Moreover, the HOMO is entirely localized to those centers where the LUMO has a node (Figure 5); hence, excitation to S_1 or T_1 entails a profound redistribution of charge within the molecule. The consequences [exchange integral $K_{\mathrm{HO,LU}} \cong 0$, unusually long wavelength S_0–S_1 absorption ($\lambda_{00} \cong 1300$ nm), very small singlet triplet splitting (possibly $E_{T_1} > E_{S_1}$ in violation of Hund's rule), high sensitivity to inductive perturbation] have been discussed previously.[40] In contrast, the HOMO in **1** is alternatingly bonding and antibonding along the periphery; hence, the perturbation promotes bond-length alternation. HOMO-LUMO excitation in **1** entails some charge transfer from the bridging double bond to the periphery but little charge reshuffling on the periphery. As a consequence, the S_0–S_1 transition of **1** occurs at a much shorter wavelength ($\lambda_{00} \cong 650$ nm; $E_{S_1} \cong 184$ kJ mol^{-1}), the singlet-triplet splitting assumes a normal value ($E_{T_1} \cong 103 \pm 20$ kJ mol^{-1} from energy-transfer experiments; hence $E_{S_1} - E_{T_1} \cong 81 \pm 20$ kJ mol^{-1}), and the S_0–S_1 transition energy is not expected to be very sensitive to inductive perturbation.

Apart from numerous theoretical papers dealing with pyracylene (**1**),[21-23,27,37,38] all of the previous experimental work was performed some 15 years ago by Trost and co-workers[2] who achieved the first synthesis and provided extensive characterization of this remarkable hydrocarbon. The simple two-step synthesis (Scheme I) of **1** reported 6 years ago by Schaden[10] has not to our knowledge been exploited prior to this work. It does involve some laborious purification and gives only a modest 5% overall yield of **1**. Nevertheless, it provides relatively easy access to **1** in up to gram quantities and, as the present work shows, in storeable form. The presence of two reactive double bonds in pyracylene invites the design of various novel compounds. Some such synthetic applications are currently being explored in our laboratories.[42]

Acknowledgment. This work was performed as part of project No. 2.835-0.88 of the Swiss National Science Foundation. We thank Dr. E. Flury, Ingenieurschule beider Basel, for providing a sample of the pyrenequinone mixture. Financial support by Ciba-Geigy, SA, Hoffmann-La Roche & Cie. SA, Sandoz SA, and the Ciba Stiftung is gratefully acknowledged.

Registry No. 1, 187-78-0; pyrene-1,6-dione, 1785-51-9; pyrene-1,8-dione, 2304-85-0.

---

(42) Soliva, A., Diplomarbeit Universität Basel, 1988.

A Laser Flash Photolysis Study of Carbonyl Ylides of Arylchlorocarbenes: Kinetics and Reversibility of the Formation, Cyclization, and Cycloaddition

Roland Bonneau and Michael T. H. Liu*,†

Contribution from the Laboratoire de Chimie Physique A, UA 348 du CNRS, Université de Bordeaux I, 33405 Talence, France. *Received May 31, 1989*

Abstract: Carbonyl ylides formed from (*p*-nitrophenyl)chlorocarbene or phenylchlorocarbene and acetone or benzaldehyde have been studied by laser flash photolysis. The rate constants for the formation of these ylides, for their cyclization to oxiranes, and for some addition reactions have been measured. Electron-withdrawing substituents on the carbene increase the rate of ylide formation and decrease the rate of cyclization. The trapping of carbonyl ylide by para-substituted benzaldehydes gave a Hammett's ρ value equal to +1.0. The dual role of benzaldehyde, first as a constituent of the ylide and second as a trapping agent, has been demonstrated. Kinetic analysis indicates that an equilibrium exists between the phenylchlorocarbene, the acetone, and the corresponding ylide, with an equilibrium constant around 0.27 M^{-1} at 300 K.

The chemistry of carbonyl ylides has been studied extensively.[1-3] Carbonyl ylides can be generated from the photolysis of oxiranes[4] and oxadiazolines[5] or from the reaction of 1-naphthylcarbene,[6] fluorenylidene,[7] and para-substituted phenylchlorocarbenes with acetone.[8-10] Also, carbonyl ylides have been generated from aldehydes and carbenes.[11] We now report a laser flash photolysis (LFP) study of phenylchlorocarbene and (*p*-nitrophenyl)chlorocarbene with acetone or benzaldehyde to give carbonyl ylides. The ylides formed in this way collapse to give oxirane or can be trapped by benzaldehydes. Rate constants for these processes are measured.

Experimental Section

3-Chloro-3-(*p*-nitrophenyl)diazirine (**1a**) and 3-chloro-3-phenyldiazirine (**1b**) were synthesized by the oxidation of the corresponding benzamidine hydrochloride in freshly prepared sodium hypochlorite in DMSO.[12] Products of ylide cyclization and benzaldehyde addition for **1a** have been reported previously.[13]

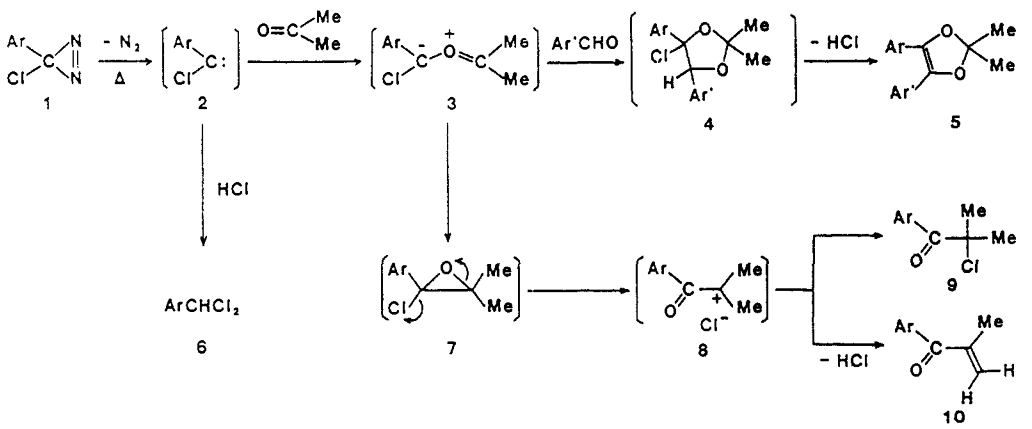
---

† On leave from University of Prince Edward Island, Charlottetown, PEI, Canada.

(1) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 572.
(2) Gill, H. S.; Landgrebe, J. A. *J. Org. Chem.* **1983**, *48*, 1051.
(3) Martin, C. W.; Landgrebe, J. A. *J. Org. Chem.* **1985**, *50*, 2050.
(4) Trozzolo, A. M.; Leslie, T. M.; Sarpotdar, R. D.; Small, R. D.; Ferraudi, G. J. *Pure Appl. Chem.* **1979**, *51*, 261.
(5) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 4260. Bekhazi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1981**, *103*, 2473.
(6) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928.
(7) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6631.
(8) Soundararajan, N.; Jackson, J. E.; Platz, M. S.; Liu, M. T. H. *Tetrahedron Lett.* **1988**, *29*, 3419.
(9) Ibata, T.; Liu, M. T. H.; Toyoda, J. *Tetrahedron Lett.* **1986**, *27*, 4383.
(10) Liu, M. T. H.; Soudararajan, N.; Anand, S. M.; Ibata, T. *Tetrahedron Lett.* **1987**, *28*, 1011.
(11) de March, P.; Huisgen, R. *J. Am. Chem. Soc.* **1982**, *104*, 4952. Huisgen, R.; de March, P. *J. Am. Chem. Soc.* **1982**, *104*, 4953.
(12) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.
(13) Ibata, T.; Toyoda, J.; Liu, M. T. H. *Chem. Lett.* **1987**, 2135.

0002-7863/90/1512-744$02.50/0

Scheme I



a: Ar = $p\text{-}NO_2C_6H_4$

b: Ar = C_6H_5

Photolysis of 1b. 1b (2×10^{-3} mol) in 2 mL of acetone was photolyzed for 40 h at 25 °C. The unreacted acetone was distilled off under reduced pressure. GC MS analysis revealed that the products were **10b** (40%), **6b** (35%), 1,4-diphenyl-1,4-dichloro-3,3-diaza-1,3-butadiene (20%), and a mixture of (*E*)- and (*Z*)-1,2-dichlorostilbene (5%, 1:1).

The laser flash photolysis setup uses a crossed-beams arrangement. The sample in a 10 × 10 mm cell was excited at 355 nm by single light pulses (200 ps, 5–50 mJ) provided by a frequency-tripled mode-locked Nd-YAG laser (Quantel). The detection system (pulsed Xe arc, monochromator, photomultiplier, and Tektronix 7912 transient recorder) has a response time of ~ 5 ns.

Results and Discussion

Thermal decomposition of **1a** in the presence of acetone yielded ketones **9a** and **10a**. These products were shown[13] to derive from the cyclization of ylide **3a** to the putative 2-chlorooxirane followed by rearrangement to give the ion pair **8a**, which yielded **9a** by recombination or **10a** by elimination of HCl. In the presence of excess acetone and a 2 molar amount of *p*-nitrobenzaldehyde, decomposition of **1a** yielded 53% (isolated) 2,2-dimethyl-4,5-bis(*p*-nitrophenyl)dioxole (**5a**; λ_{max} = 440 nm), 19% *p*-nitrobenzal dichloride (**6a**), and 4% 2-chloro-2-methyl-3-(*p*-nitrophenyl)-3-propanone (**9a**) (Scheme I).

LFP of **1a** in isooctane produced the known transient spectrum (λ = 320 nm) for the carbene **2a**.[14] In the presence of acetone, a new transient is formed (λ_{max} = 590 nm; Figure 1) and is attributed to the ylide **3a**. Our results indicate that the lifetime of **3a** in isooctane is independent on the acetone concentrations. Therefore, both the decomposition of **3a** to give back carbene and acetone and the cycloaddition of **3a** with acetone are not important: this observation is consistent with our previous relative measurements indicating that the formation of carbonyl ylide from carbene **2a** and acetone is not reversible[10] and that the system is well described by the following mechanistic scheme where $k_- \ll k_{cy} \ll k_y$[acetone]:

$$\begin{tikzcd}
\text{diazirine} \arrow[r, "h\nu"] & \text{carbene + acetone} \arrow[r, shift left, "k_y"] \arrow[dl, "k_1"] & \text{ylide} \arrow[l, shift left, "k_-"] \arrow[d, "k_{cy}"] \\
\text{products} & & \text{oxirane}
\end{tikzcd}$$

The lifetime of ylide **3a** (1.35 μs at room temperature in a degassed isooctane solution) is controlled by cyclization to the corresponding oxirane; thus, $k_{cy} = 7.40 \times 10^5\ s^{-1}$ at room temperature.

Similarly, LFP of **1b** in isooctane–acetone mixture gives rise to a transient absorption in the 400–580-nm region, with a maximum absorption around 450 nm (see Figure 1). This absorption, which is not observed in neat isooctane solvent, is assigned to the carbonyl ylide **3b**. Growth and decay rate constants, k_g and k_d, have been determined by computer fitting the curves OD $= f(t)$ with the following expression where A is a proportionality factor:

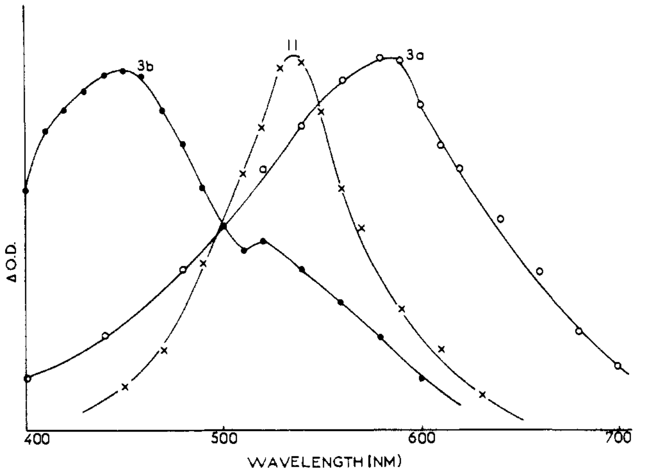


Figure 1. Absorption spectra for carbonyl ylides **3a** in isooctane + 2 M acetone, **3b** in neat acetone, and **11** in isooctane + 1 M benzaldehyde.

$$OD = A\ [\exp(-k_d t) - \exp(-k_g t)] \tag{1}$$

The values of k_g, and OD_{max}, the observed maximum absorbance, are plotted as a function of [acetone] in Figure 2. Clearly, the simplified mechanism used above cannot account for the results obtained since such a mechanism predicts that on changing [acetone] from 1.2 to 13.6 M, k_d, which is equal to k_{cy}, should be constant whereas $k_g = k_1 + k_y$[acetone] would change by, at least, a factor of 10. Therefore, we consider the above mechanism in which the ylide is reversibly formed. In this case the ylide concentration (Yl) as a function of time is given by

$$Yl(t) = C_0[k_y[\text{acetone}]/(\lambda_2 - \lambda_1)]\ [\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \tag{2}$$

where

$$\lambda_{1,2} = 0.5[(X + Y) \pm \{(X - Y)^2 + 4k_- k_y[\text{acetone}]\}^{1/2}] \tag{3}$$

with $X = (k_y[\text{acetone}] + k_1)$, $Y = (k_{cy} + k_-)$ and C_0 being the initial carbene concentration. Comparing eq 1 and 2, it may be seen that $\lambda_1 = k_d$ and $\lambda_2 = k_g$, and from eq 3, the extrapolation of k_d at [acetone] = 0 gives the value of $k_1 \approx 4 \times 10^5\ s^{-1}$. From eq 3 one gets the following relations:

$$(\lambda_1 + \lambda_2) = (k_d + k_g) = k_y[\text{acetone}] + (k_1 + k_{cy} + k_-) \tag{4}$$

$$(\lambda_1\lambda_2) = (k_d k_g) = k_1(k_{cy} + k_-) + k_{cy}k_y[\text{acetone}] \tag{5}$$

$$(k_g - k_d)^2 = k_y^2[\text{acetone}]^2 + 2k_y(k_1 + k_- - k_{cy})[\text{acetone}] + (k_{cy} + k_- - k_1)^2 \tag{6}$$

---

[14] Bonneau, R.; Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1989**, 510.

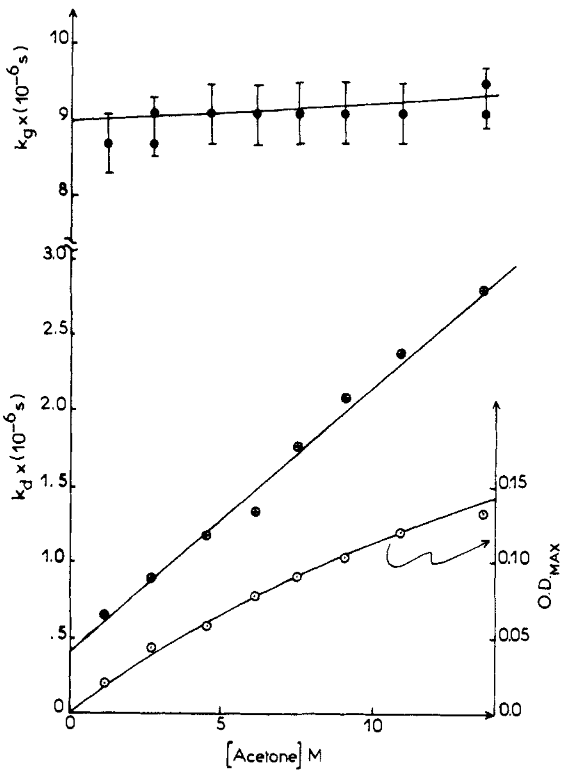


Figure 2. Effect of [acetone] on the rate constants for growth (k_g) and decay (k_d) and on the observed maximum absorbance (OD_{max}) of the carbonyl ylide "phenylchlorocarbene + acetone". The curve OD_{max} vs [acetone] is calculated from eq 2. Temperature, 300 K; observation at 450 nm.

From the slope and/or the extrapolated intercept of the plots of eq 4–6 vs [acetone], one gets the value of the various rate constants:

$$k_y = 2.0 \pm 0.3 \times 10^5\ M^{-1}\ s^{-1} \qquad k_- = 7.5 \pm 1 \times 10^5\ s^{-1}$$

$$k_{cy} = 8.1 \pm 0.1 \times 10^6\ s^{-1}$$

According to eq 2, $Yl(t)$ reaches a maximum at $t = \ln(\lambda_1/\lambda_2)/(\lambda_1 - \lambda_2)$ and the calculated values of Yl(max) can be compared to OD_{max}, after correction by a scaling factor to account for the product ϵC_0, ϵ being the extinction coefficient of the ylide. The excellent agreement between the experimental and the calculated variations of k_d, k_g, and OD_{max} as a function of [acetone] in Figure 2 strongly supports the proposed mechanism and the values assigned to the various rate constants.

When the present data are compared with those previously published[8,10] for k_y and k_{cy}, it is clear that electron-withdrawing substituents in the para position increase the rate of ylide formation and decrease the rate of epoxide formation. The values for k_y are 35, 15, 5, and 0.2 × $10^6\ M^{-1}\ s^{-1}$ and those for k_{cy} are 0.74, 2–5, 2–5, and 8 × $10^6\ s^{-1}$ for NO_2, CF_3, Cl, and H, respectively.

The effect of temperature on the ylide lifetime was examined over the 10–80 °C temperature range. Least-squares analysis of data in Figure 3 gives the following kinetic parameters: $E_a = 5.90 \pm 0.20$ and 2.1 ± 0.27 kcal/mol and $\log A = 10.30 \pm 0.15$ and 7.40 ± 0.20 for **3a** and **3b**,[15] respectively. For **3a**, these parameters are those for the cyclization process. For **3b**, since k_d is a complex expression of several rate constants, these parameters have no real significance. The kinetics parameters for the same ring closure reaction have already been reported for other carbonyl ylides: $E_a = 1.5$ kcal/mol and $\log A = 6.9$ for the "1-naphthylcarbene + acetone" ylide[6] and $E_a = 10.96$ kcal/mol and $\log A = 13.26$ for the "fluorenylidene + acetone" ylide.[7] The very low A factor in the former may be related to the triplet character of the parent carbene but, as shown in the case of **3b**, reversibility of the ylide formation can also lead to low A factors.

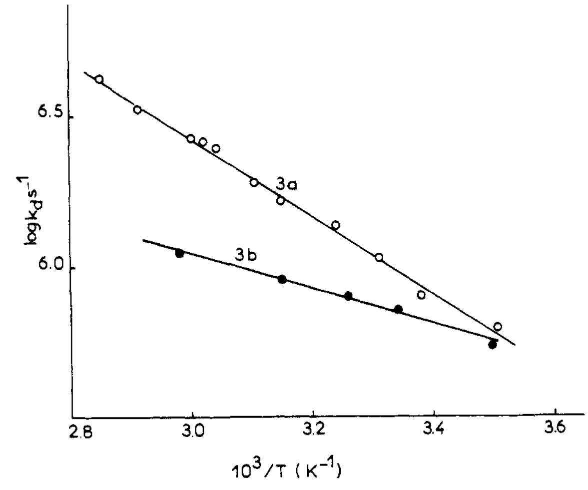


Figure 3. Arrhenius plots of k_d for ylides **3a** and **3b**. The derived kinetic parameters for **3a** relate to the cyclization process whereas, for **3b**, k_d is complex (see text).

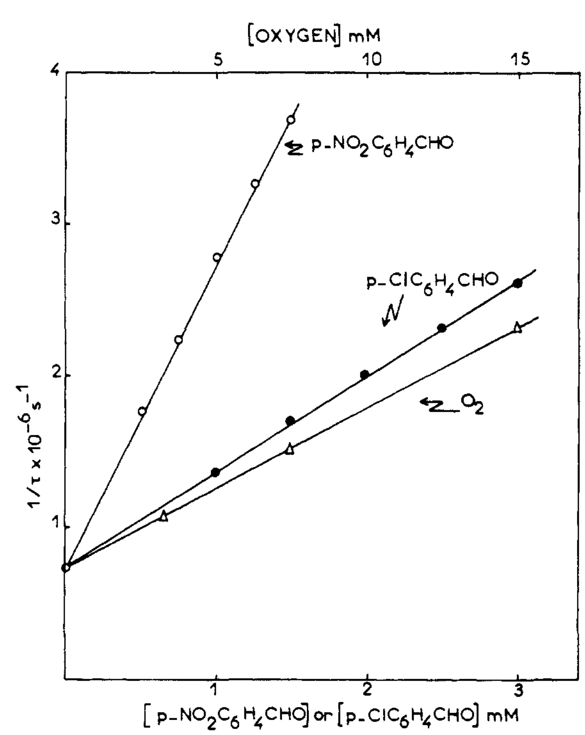


Figure 4. Reciprocal lifetime of ylide **3a** vs concentration of various quenchers.

Ylide **3a** can give addition reactions to many reactants. For instance, it is quenched by oxygen, olefins, and benzaldehydes. The reciprocal lifetime of the ylide **3a** vs [oxygen] is displayed in Figure 4. The slope of the plot yields $k_q = 1.1 \pm 0.1 \times 10^8 M^{-1}\ s^{-1}$. Diethyl fumarate (DEF) quenches the ylide **3a** with a rate constant equal to $6.4 \times 10^8\ M^{-1}\ s^{-1}$. Recall that the fluorenylidene–acetone ylide is similarly quenched by oxygen and DEF[7] with rate constants respectively equal to 7.2 ± 0.4 and $4.4 \pm 0.3 \times 10^7\ M^{-1}\ s^{-1}$.

The reactions of the ylide **3a** with benzaldehyde, *p*-chlorobenzaldehyde, and *p*-nitrobenzaldehyde have been examined. The plots of the reciprocal lifetime of the ylide as a function of the concentration of the aldehyde yielded the following values: 3.50 ± 0.1, 6.16 ± 0.1, and $19.6 \pm 0.1 \times 10^8\ M^{-1}\ s^{-1}$ for the quenching rate constant of ylide **3a** by benzaldehyde, *p*-chlorobenzaldehyde, and *p*-nitrobenzaldehyde, respectively. Representative plots for the latter two reactions are shown in Figure 4. Electron-withdrawing substituents on benzaldehyde increase the rate of reaction, in agreement with the increase in yields of dioxoles **5a** observed

---

[15] Measured with [acetone] ≈ 2 M. From the analytical expression of k_d, the temperature dependence is expected to depend on [acetone].

in product analysis after photolysis under continuous irradiation. The slope of the Hammett plot of log k vs σ_p is equal to +1.0; the positive value of σ is consistent with the electrophilic addition of the benzaldehyde to the carbonyl ylide. Theoretically, the decay of ylide **3a** must be equal to the growth of dioxole **5a** if HCl elimination is rapid. Attempts have been made to follow the growth of **5a**. However, no transient spectrum was observed at 440 nm during the few milliseconds following the excitation. On the other hand, the failure to isolate dioxolane **4a** under medium-pressure liquid chromatography on silica gel suggests that the elimination of HCl from **4a** occurs within a few minutes at room temperature.

In the absence of acetone, the laser photolysis of **1a** in isooctane in the presence of benzaldehyde produced a new transient absorption (λ_{max} = 530 nm). This transient absorption is assigned to the carbonyl ylide **11** formed by reaction of carbene **2a** with benzaldehyde. Measurement of the rate of growth of the absorption at 530 nm as a function of [benzaldehyde] yielded the rate constant for ylide formation, $k = 1.1 \times 10^9$ M^{-1} s^{-1}. The ylide **11** is subsequently quenched by benzaldehyde, as shown by the dependence of its decay time on [benzaldehyde] but, since this decay does not fit a first-order law, the quenching rate constant is not easily extracted from the kinetic data. Thus, benzaldehyde plays a double role, first as a constituent of a carbonyl ylide and then as a dipolarophile in the trapping of the ylide. Huisgen and de March[11] reported a similar mechanism to explain the formation of the diastereoisomeric 1,3-dioxolanes and oxirane in the thermal reaction of dimethyl diazomalonate with an excess of benzaldehyde.

Registry No. **1a**, 39184-67-3; **1b**, 4460-46-2; **3a**, 111286-57-8; **3b**, 124125-69-5; **5a**, 115107-28-3; **6a**, 619-78-3; **9a**, 83846-29-1; **11**, 124125-70-8; DEF, 623-91-6; MeCOMe, 67-64-1; p-$NO_2C_6H_4CHO$, 555-16-8; O_2, 7782-44-7; C_6H_5CHO, 100-52-7; p-ClC_6H_4CHO, 104-88-1.

Photoinduced Intramolecular Proton Transfer as the Mechanism of Ultraviolet Stabilizers: A Reappraisal

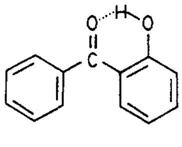
**Javier Catalán,[*,†] Fernando Fabero,[†] M. Soledad Guijarro,[†] Rosa M. Claramunt,[*,‡]
M. Dolores Santa María,[‡] M. de la Concepción Foces-Foces,[§] Felix Hernández Cano,[§]
José Elguero,[⊥] and Roberto Sastre[||]**

Contribution from the Departamento de Química, Física, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain, Departamento de Química Orgánica, UNED, 28040 Madrid, Spain, U.E.I. de Cristalografía, Instituto de Química Física "Rocasolano", CSIC, 28006 Madrid, Spain, Instituto de Química Médica, CSIC, 28006 Madrid, Spain, and Instituto de Ciencia y Tecnología de Polímeros, CSIC, 28006 Madrid, Spain.

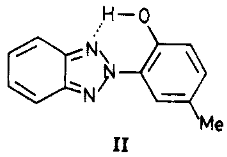
Received June 29, 1989

Abstract: Evidence based on theoretical calculations and photophysical experiments is presented to show that, contrary to general belief, the photostability of 2-(2′-hydroxy-5′-methylphenyl)benzotriazole (Tinuvin P) cannot be explained as being due to an excited-state intramolecular proton transfer (ESIPT) through the intramolecular hydrogen bond (IMHB). Support for this conclusion comes from a related study on several members of a new family of photostable compounds, namely the 1-(2′-hydroxyphenyl)pyrazoles, which were obtained by the reaction of pyrazole and of 3,5-dimethylpyrazole with benzoquinone. The structures of these pyrazole derivatives, namely 2,3-bis(3′,5′-dimethylpyrazol-1′-yl)-, 2,3-bis(pyrazol-1′-yl)-, 2-(pyrazol-1′-yl)-, and 2,5-bis(pyrazol-1′-yl)-1,4-dihydroxybenzene (**1**, **2**, **3**, and **4**, respectively) were established by spectroscopic techniques and X-ray crystallography. Both derivatives **3** and **4** possess a strong intramolecular hydrogen bond and are reasonably photostable; derivatives **1** and **2** appear, however, to possess only a weak intramolecular hydrogen bond. **1** and **3** pack in helical systems, **4** does it with intercrossing stacking, and **2**·H_2O has a three-dimensional network involving water molecules.

An important class of photostabilizers are the ultraviolet absorbers or light screeners; these colorless or nearly colorless organic compounds are able to protect polymers and other light-sensitive materials from damage caused by the ultraviolet component of sunlight and various kinds of artificial light. In the chemical structure of such compounds, it is usual[1] to find a phenolic group which is intramolecularly hydrogen bonded (IMHB) to a heteroatom as oxygen or nitrogen of the same chromophore. Important families of such photostabilizers are the 2-hydroxybenzophenones (represented by the parent compound (I)) and the 2-(2′-hydroxyphenyl)benzotriazoles (represented by the methyl derivative (II) commonly known as Tinuvin P).



I



II

In order to explain the large Stokes shift (11 000 cm^{-1}) observed in the fluorescence spectrum of methyl salicylate (III), Weller[2] proposed the so-called ESIPT (excited-state intramolecular proton transfer) model (IIIb → IIIc), with proton transfer taking place along the IMHB.

This model has led some authors[1,3-7] to suggest that the photostability of such compounds is due to a rapid nonradiative deactivation of the quinonoid form IIIc, due to the dramatic approximation of the electronic states implicated in the intramolecular proton transfer. This process regenerates the original form IIIa and confers upon methyl salicylate a high stability to ultraviolet light.

---

[*] Authors to whom correspondence should be addressed.

[†] Departamento de Química, UAM.

[‡] Departamento de Química Orgánica, UNED.

[§] Instituto Rocasolano, CSIC.

[⊥] Instituto de Química Médica, CSIC.

[||] Instituto de Ciencia y Tecnología de Polímeros, CSIC.

(1) Heller, H. J. *Eur. Polym. J. Suppl.* **1969**, 105.

0002-7863/90/1512-747$02.50/0 © 1990 American Chemical Society