ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 119 (1998) 165–170

Journal of Photochemistry and Photobiology A:Chemistry

Photochemistry of cyclic vicinal tricarbonyl compounds. [2+2] Photocycloaddition of 1,2,3-indanetrione to electron rich olefins

J.C. Netto-Ferreira*, M.T. Silva, F.P. Puget

Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Antiga Rodovia Rio-São Paulo km 47, Seropédica, Rio de Janeiro, CEP 23851-970, Brazil

Received 30 April 1998; received in revised form 27 July 1998; accepted 31 August 1998

Abstract

Photolysis of 1,2,3-indanetrione (**1**) in dichloromethane, in the presence of 2,3-diphenyl-1,4-dioxene, leads to the formation of the corresponding oxetane **6**, through a Paterno-Büchi reaction. The irradiation of **1** in the presence of 2-methyl-2-butene gives, in addition to the oxetane **7**, products arising from an allylic hydrogen abstraction process, i.e. **E-8** and **9**. On the other hand, in the presence of 2,4,4-trimethyl-1-pentene, the only product formed, i.e. **12**, results from an allylic hydrogen abstraction reaction from the primary center. The regioselectivity found in some of these reactions was associated to strong steric effects in the approach between triketone triplet and the olefin. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Triketones; 1,2,3-indanetrione; Photolysis; Paterno-Büchi; Hydrogen abstraction

1. Introduction

In spite of the fact that the synthesis of 1,2,3-indanetrione (**1**) was reported more than 50 years ago [1], surprisingly little is known about its photochemical behavior. The photochemistry of **1** was recently examined by us [2] in solution at room temperature by steady state and laser flash photolysis. Its triplet state ($\tau = 6.5$ µs, $\lambda_{max} = 360$ and 570 nm, in dry acetonitrile) reacts preferentially via a α-cleavage process followed by a considerably slower loss of carbon monoxide, resulting in the formation of *trans*-biphthalyl (**4**) and the diisocoumarin **5**, through the dioxacarbene **2** and/or the biradical **3** (Scheme 1).

Recently the photochemistry of the trione **1** under high-intensity (laser jet) conditions has been investigated. Thus, photolysis of **1** resulted in a complex mixture of products from which 1,2-benzocyclobutenedione was the only product arising from the high-intensity irradiation [3].

Triplet **1** shows a remarkably fast hydrogen abstraction rate constant from 1,4-cyclohexadiene or toluene ($k_r = 1.4 \times 10^6\ M^{-1}\ s^{-1}$, in both cases). This behavior can be explained by assuming that the vicinal carbonyls coplanar to the ketyl radical play an important role on its stabilization [2].

In this communication we are able to show for the first time that the photochemical reaction of 1,2,3-indanetrione (**1**) with electron rich olefins leads to product formation by both photocycloaddition and allylic hydrogen abstraction reactions.

2. Experimental

2.1. Materials

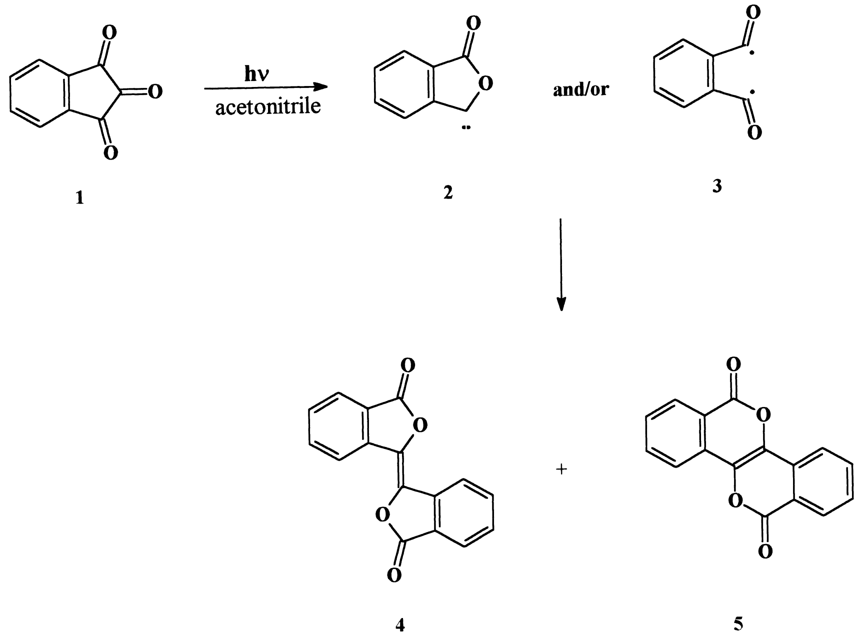
The solvents employed were Aldrich Spectrograde and were used as received. The olefins 2,4,4-trimethyl-1-pentene and 2-methyl-2-butene were purchased from Aldrich. 2,3-Diphenyl-1,4-dioxene was synthesized according to reference [4]. Maleic anhydride, dimethyl fumarate, 1,1-diphenylethylene, acenaphthylene, and diastereoisomerically pure *cis*- or *trans*-stilbene were purchased from Aldrich.

1,2,3-Indanetrione was synthesized by heating ninhydrin (Aldrich) in the presence of excess thionyl chloride under reflux [5]. Alternatively, **1** was prepared by sublimative dehydration of ninhydrin [6]. In both cases a melting point of 254–255°C was measured (Ref [5] = 255°C). After preparation, the red–violet crystals were kept in sealed ampoules under reduced pressure.

---

*Corresponding author.

PII: S1010-6030(98)00393-1



Scheme 1.

2.2. General techniques

GC analysis were carried out on a Varian model 2400 capillary gas chromatograph employing a 15 m J and W bonded phase vitreous silica FFAP column, and under the following conditions: T_{column} from 50°C to 240°C, at 40°C min^{-1}; $T_{\text{detector}} = 300°\text{C}$; $T_{\text{injector}} = 250°\text{C}$. GC/MS analysis were carried out on a Hewlett-Packard model 5970/5890 employing a 50 m J and W bonded phase vitreous silica HP-54 column. Main peaks were obtained by electron impact with the spectrometer operating at 70 eV.

^{1}H- and ^{13}C-NMR spectra were recorded in a Bruker AC 200 spectrometer (^{1}H: 200 MHz; ^{13}C: 50.3 MHz) in $CDCl_3$ and using tetramethylsilane as the internal standard.

Infrared spectra were obtained in a model 1420 Perkin-Elmer spectrophotometer in CCl_4 liquid film.

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

2.3. Product studies

The irradiations were done in a Rayonet with 9 RPR-3000 lamps, at room temperature. Typical samples were 100 ml of a 10^{-2} M solution of **1** in dichloromethane containing a large excess of the olefin. Samples were contained in Pyrex tubes and deaerated by bubbling oxygen-free nitrogen in a dark room due to the high photochemical reactivity of the triketone. The solution containing **1** and the corresponding olefin was irradiated until the green color of the original dichloromethane solution became pale yellow (less than 1 h irradiation). The products were isolated by preparative thin-layer chromatography (silica, and chloroform : acetone – 9 : 1 – as eluent). In the case where *cis*- or *trans*-stilbene was the olefin employed a set of 16 RPR-3500 lamps were used. At this wavelength these two olefins have molar extinction coefficient close to zero [7]. For quantum yield determination, the photofragmentation of valerophenone in benzene was used as an actinometer, with product distribution being analyzed by GC and using *n*-dodecane as an internal standard ($\phi = 0.3$ for acetophenone formation [8]).

Low temperature irradiations (at $\sim -10°\text{C}$) were performed in an Ace Glass immersion well by using a 450 W Hanovia immersion lamp. The same product distribution was observed when irradiations at room temperature were compared with those at $\sim -10°\text{C}$.

2.3.1. Spectroscopic and spectrometric data for products **6, 7, E-8, 9** *and* **12**

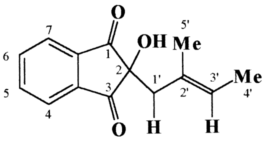
6: ^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm): 8.07–8.02 (m, aromatic protons); 7.56–7.24 (m, aromatic protons); 4.19–4.16 (m, CH_2); 4.13–4.10 (m, CH_2). ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ (ppm): 133.52; 133.12; 130.47; 129.67; 129.18; 128.66; 128.07; 125.55; 65.72; 62.70. IR (KBr): ν (cm^{-1}): 1719 (C=O); 1602; 900; 720. MS *m/z* (rel. int.): 398 ($M^{+\bullet}$, absent); 148 (23); 106 (79); 105 (100); 77 (98).

7: ^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm): 7.84–7.44 (m, aromatic protons); 1.94 (quartet, CH, $J = 7.1$ Hz); 1.29 (s, CH_3); 1.14 (s, CH_3); 1.01 (d, CH_3, $J = 7.1$ Hz). ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ (ppm): 201.56 (C=O); 140.79; 136.90; 124.06; 89.64; 86.22; 48.65; 27.96; 23.94; 7.92. IR (KBr): ν (cm^{-1}): 1748 (C=O); 1701 (C=O); 1260; 984. MS *m/z* (rel. int.): 230 ($M^{+\bullet}$, 100); 215 (70); 172 (20); 162 (17); 161 (61); 160 (40); 133 (21); 132 (21); 105 (59); 104 (50); 77 (28); 76 (17).

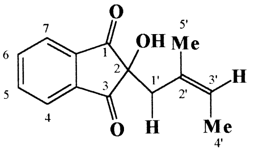
E-8: ^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm): 7.96–7.89 (m, aromatic protons); 7.89–7.82 (m, aromatic protons);

5.27 (m, olefinic proton); 2.56 (s, CH_2); 1.39 (d, CH_3); 1.38 (s, CH_3). ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ (ppm): 199.86 (C=O); 143.76; 141.13; 136.28; 126.66; 123.48; 78.03; 46.65; 16.90; 13.50. IR (KBr): ν (cm^{-1}): 3445 (OH); 1741 (C=O); 1721 (C=O); 1647 (C=C). MS *m/z* (rel. int.): 230 ($M^{+\cdot}$, absent); 162 (93); 160 (23); 133 (21); 132 (61); 105 (71); 104 (100); 77 (35); 76 (88).

The *E* assignment for product **8** was made by NOE (Nuclear Overhauser Effect) experiments. Irradiation of H-3′ at 5.27 ppm clearly shows its interaction with H-1′ (2.56 ppm) and H-4′ (1.39 ppm), evidencing the close proximity between protons H-3′ and H-1′.



***E*-8**



***Z*-8**

9: ^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm): 7.96–7.89 (m, aromatic protons); 7.89–7.82 (m, aromatic protons); 4.79 (s, =CH_2); 2.80 (q, CH, $J = 7.2$ Hz); 1.54 (s, CH_3); 1.07 (d, CH_3, $J = 7.2$ Hz). ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ (ppm): 199.53 (C=O); 143.59; 140.38; 136.28; 123.48; 116.21; 79.46; 47.59; 20.21; 13.14. IR (KBr): ν (cm^{-1}): 3445 (OH); 1741 (C=O); 1721 (C=O); 1647 (C=C). MS *m/z* (rel. int.): 230 ($M^{+\cdot}$, 100); 212 (14); 162 (23); 161 (19); 160 (10); 133 (14); 132 (64); 105 (22); 104 (42); 77 (26); 76 (20); 69 (45).

12: ^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm): 8.05–7.92 (m, aromatic protons); 4.73 (m, vinylic proton); 4.54 (m, vinylic proton); 2.72 (s, CH_2); 1.64 (s, CH_2); 0.80 (s, CH_3). ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ (ppm): 201.33 (C=O); 141.87; 141.63; 137.29; 123.84; 118.94; 78.32; 50.03; 44.44; 32.04; 29.80; IR (KBr): ν (cm^{-1}): 3459 (OH); 1748 (C=); 1714 (C=O); 1636 (C=C). MS *m/z* (rel. int.): 272 ($M^{+\cdot}$, absent); 162 (93); 160 (12); 146 (63); 134 (26); 133 (19); 132 (37); 112 (28); 105 (63); 104 (81); 77 (34); 76 (53); 57 (100).

3. Results and discussion

Photochemical irradiation of 1,2,3-indanetrione (**1**) ($E_T = 42$ kcal mol^{-1}) [2,9] in the presence of 2,3-diphenyl-1,4-dioxene, a considerably electron rich olefin, leads to the formation of the oxetane **6** with quantum yield close to unity. This product results from a [2 + 2] photocycloaddition reaction between the excited triketone and the olefin, probably through the 1,4-biradical formed by the attack of the electrophilic-excited carbonyl oxygen to the olefin double bond (Scheme 2).

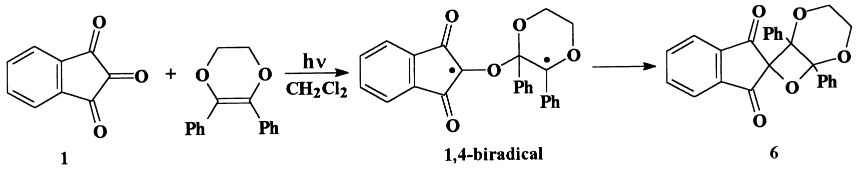
When the irradiation was performed with diastereoisomerically pure *cis*- or *trans*-stilbene, only olefin isomerization could be observed. In this case the same *cis*/*trans* ratio was obtained, independently of the starting isomer. Direct energy transfer from triplet triketone to the olefin is not possible due to considerably large difference in triplet energy between **1** and *cis*- or *trans*-stilbene, making this energy transfer process endothermic by at least 15 kcal mol^{-1} for the *cis* isomer and 8 kcal mol^{-1} for the *trans* [7].

The quantum yield for oxetane formation in the irradiation of 1,2,3-indanetrione and 2,3-diphenyl-1,4-dioxene was measured in solvents of decreasing polarity (acetonitrile, dichloromethane and benzene) and in all cases a value close to unity was found. This seems to indicate that a radical anion/radical cation intermediate mechanism probably is not involved in this reaction. It is worth noting that quantum yields close to unity were also measured for the reaction between 1,2,3-indanetrione and 2-methyl-2-butene in the same solvents. These results are fully in accordance with laser flash photolysis experiments, from which rate constants for the reaction of triplet 1,2,3-indanetrione with these olefins were obtained and with the same order of magnitude ($k_r = 7 \times 10^6\ M^{-1}\ s^{-1}$ for the dioxene and $k_r = 4 \times 10^6\ M^{-1}\ s^{-1}$ for 2-methyl-2-butene) [10].

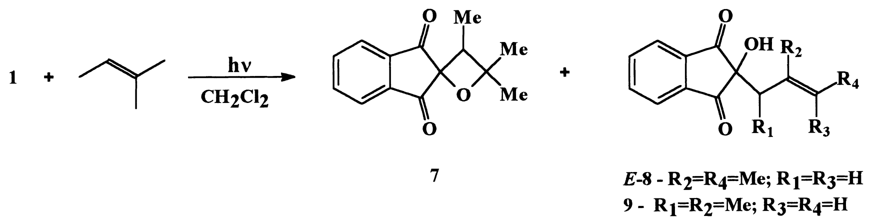
To account for these results we can suggest the formation of an exciplex prior to the intermediate 1,4-biradical (Scheme 2), despite the fact that the involvement of this kind of reactive intermediate in Paterno–Büchi reactions is still controversial. Such an exciplex is usually considered to possess a rather small amount of charge transfer character, which is in agreement with the results described above [11–13]. However, this CT character appears to play a significant role in the decay of the exciplex to ground-state olefin and ketone as well as in its collapse to a radical pair or to a 1,4-biradical.

Photolysis of **1** in the presence of olefins containing electron acceptor substituents such as maleic anhydride or dimethyl fumarate did not result in product formation. A similar result was found with di-substituted olefins bearing no allylic hydrogens, such as 1,1-diphenylethylene or acenaphthylene.

On the other hand, irradiation of **1** in the UV region and in the presence of the tri-substituted olefin 2-methyl-2-butene,



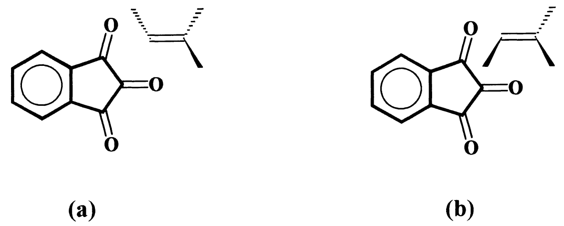
Scheme 2.



Scheme 3.

in dichloromethane, leads to formation of the oxetane **7** (18%), as well as to products formed by an initial hydrogen abstraction from the olefin, *i.e.* **E-8** (47%) and **9** (35%) (Scheme 3). Product **9** was formed through a coupling reaction between the ketyl radical derived from 1,2,3-indanetrione, by hydrogen abstraction from 2-methyl-2-butene, and the 2-methyl-2-buten-1-yl radical, a resonant form of the initially formed 2-methyl-1-buten-3-yl radical. Alternatively, **9** could also be formed through a hydrogen abstraction reaction by triplet **1** from the methyl group in C-2. However, in this case formation of **Z-8** should also be observed.

It is worth noting that products arising from hydrogen abstraction of the allylic hydrogen bonded to C-4 in 2-methyl-2-butene were not detected by the spectroscopic and spectrometric methods employed in this work. Similarly, the main product expected from a hydrogen abstraction from the methyl group in C-2 and *anti* to the vinylic hydrogen of 2-methyl-2-butene, i.e. **Z-8**, was not observed. This can be due to a strong steric interaction between the C-1 (or C-3) carbonyl oxygen in **1** and one of these two methyl groups. Fig. 1 clearly shows that in the approach topology depicted in (**a**) there is a weak interaction between the vinylic hydrogen and the C-1 carbonyl oxygen. However, in Fig. 1(b) the strong steric hindrance caused by the proximity of the C-4 methyl group of the olefin and the C-1 carbonyl oxygen makes this an unfavorable approach. Thus, the complete absence of products resulting from hydrogen abstraction from the methyl group at C-4, as well as the diastereospecificity for the formation of **8,** definitely rule out the approximation for the interaction between 1,2,3-indanetrione and 2-methyl-2-butene depicted in Fig. 1(b). A similar steric effect was invoked to explain the difference in reactivity and in regioselectivity in the thermal *ene* reaction between **1** and olefins [14].



(a) **(b)**

Fig. 1. Possible approximations for the interaction between 1,2,3-indanetrione triplet and 2-methyl-2-butene.

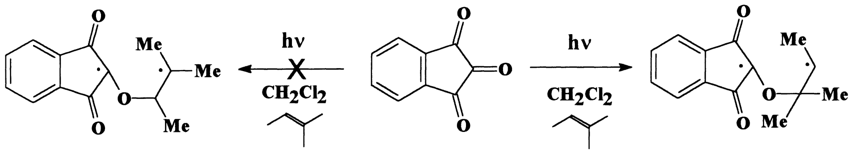
As for the previous case, product formation can be explained by considering the involvement of an initial exciplex which decays either to give a 1,4-biradical, precursor of the oxetane **7**, or to form a radical pair by an intramolecular hydrogen abstraction, which is responsible for the formation of products **E-8** and **9** (Scheme 3).

It is important to note that in this case oxetane formation did not follow the established mechanism that predicts the involvement of the more stable 1,4-biradical (Scheme 4) [15]. The formation of the less stable biradical, i.e. **10**, could be associated to the severe steric hindrance between the excited triketone and the olefin, as described above (Fig. 1(b)). This would prevent the more common symmetry allowed perpendicular approximation carbonyl-double bond to occur, leading to biradical **11**, and consequently to the unexpected regiospecificity of the corresponding oxetane **7**. Thus, it is proposed that the same topology approach is responsible for both oxetane formation and hydrogen abstraction reaction.

To confirm that steric hindrance is controlling the way cyclic vicinal triketones interacts with olefins leading to allylic hydrogen abstraction reactions, the photochemistry of 1,2,3-indanetrione (**1**) in the presence of a less hindered di-substituted olefin was investigated. Thus, irradiation of a dichloromethane solution of **1** and 2,4,4-trimethyl-1-pentene leads to the formation of **12** as the only product (Scheme 5), which arises from an allylic hydrogen abstraction reaction from the primary center. The absence of [2 + 2] photocycloaddition products clearly indicates that only electron-rich olefins, i.e. substituted at least by three alkyl groups or containing electron donor substituents, are able to lead to oxetane formation.

The fact that hydrogen abstraction from the secondary allylic hydrogen was not observed is again probably due to steric factors preventing the approximation between the excited carbonyl and the center bearing this hydrogen. Fig. 2 shows possible approximation modes between excited 1,2,3-indanetrione and this olefin, from which one can conclude that topology in (**a**) strongly favor the primary allylic hydrogen abstraction.

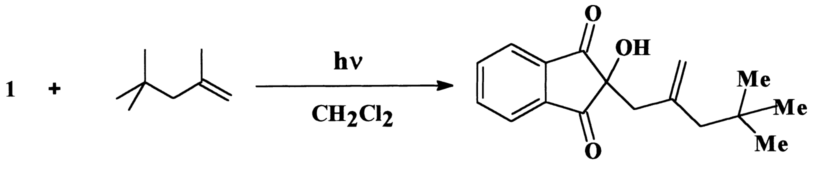
Cyclic vicinal tricarbonyl compounds can react thermally with olefins through an *ene* addition reaction [14,16]. These reactions are done at moderate temperatures (~100°C) and products are structurally similar to those obtained by allylic hydrogen abstraction in the photochemical reaction. To confirm that the products obtained in our case are only



11

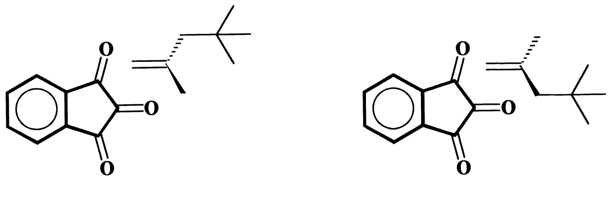
10

Scheme 4.



12

Scheme 5.



(a) (b)

Fig. 2. Possible approximations for the interaction between indanetrione triplet and 2,4,4-trimethyl-1-pentene.

derived from the photochemical reaction, low temperature experiments were performed. Thus, the irradiation of **1** in presence of olefins bearing allylic hydrogens, i.e. 2-methyl-2-butene and 2,4,4-trimethyl-1-pentene, was performed at ~−10°C. In both cases the same products were obtained, and for the case of the former olefin, in the same ratio. Therefore, these experiments confirm the photochemical nature of these reactions. Furthermore, the formation of product **9** on the irradiation of **1** in the presence of 2-methyl-2-butene clearly indicates the involvement of the 2-methyl-2-buten-1-yl radical in this reaction, which is not compatible with a concerted reaction such as the *ene* addition.

Unlike *o*-quinones such as phenanthrenequinone [17] or 1,2-naphthoquinone [18], no evidence was found for the formation of products arising from a [4 + 2] photocycloaddition in any of the reactions between triplet **1** and olefins. On the other hand, the regioselectivity found in α-diketones is usually a consequence of the difference on the electrophilicity between the two groups belonging to the α-dicarbonyl system [18].

It is well known that cyclic vicinal tricarbonyl compounds show very unfavorable electrostatic interactions between their carbonyl groups [19]. The observed exclusive reactivity of the central carbonyl in the photolysis of 1,2,3-indanetrione (**1**) in the presence of olefins must be a consequence of the relieving to some extent of such interactions.

In conclusion, it was clearly shown for the first time that the cyclic vicinal triketone 1,2,3-indanetrione (**1**) has a photochemical behavior towards olefins similar to that of monoketones. Moreover, product formation in the photolysis of 1,2,3-indanetrione (**1**) and olefins, either from hydrogen abstraction or [2 + 2] photocycloaddition, is strongly dependent on steric effects. Further work is currently in progress aiming to show the generality of this behavior with this and other cyclic vicinal tricarbonyl compounds.

Acknowledgements

A financial grant from the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) is gratefully acknowledged. We thank Dr. R. Braz-Filho for fruitful discussions regarding product identification.

References

[1] A. Schönberg, A. Mustafa, J. Chem. Soc. (1947) 997.
[2] J.C. Netto-Ferreira, J.C. Scaiano, Photochem. Photobiol. 54 (1991) 17.
[3] W. Adam, W.S. Patterson, J. Org. Chem. 60 (1995) 7769.
[4] R.K. Summerbell, D.R. Berger, J. Am. Chem. Soc. 81 (1959) 639.
[5] A. Schönberg, R. Moubascher, J. Chem. Soc. (1943) 71.
[6] A.R. Lepley, J.P. Thelman, Tetrahedron 22 (1966) 101.
[7] S.L. Murov, Handbook of Photochemistry, Marcel Dekker, New York, 1973.
[8] P.J. Wagner, P.A. Kelso, A.E. Kempainen, J.M. McGrath, H.N. Scott, R.G. Zepp, J. Am. Chem. Soc. 94 (1972) 7506.
[9] J. Roy, S. Bhatthacharya, D. Majumder, S.P. Bhattacharya, J. Photochem. Photobiol. A: Chem. 109 (1997) 133.
[10] J.C. Netto-Ferreira, M.T. Silva, N.C. de Lucas, unpublished results.
[11] R.A. Caldwell, S.P. Jones, J. Am. Chem. Soc. 91 (1969) 518412.

[12] R.A. Caldwell, J. Am. Chem. Soc. 92 (1970) 1439.

[13] R.A. Caldwell, G.W. Sovocool, R.P. Gajewski, J. Am. Chem. Soc. 95 (1973) 2549.

[14] G. Bryon Gill, M.S.Hj. Idris, K.S. Kirollos, J. Chem. Soc., Perkin Trans. 1 (1992) 2355.

[15] N.E. Shore, N.J. Turro, J. Am. Chem. Soc. 97 (1975) 2482.

[16] G. Bryon Gill, M.S.Hj. Idris, Tetrahedron 49 (1993) 219.

[17] S. Farid, K.-H. Scholz, J. Chem. Soc., Chem. Commun. (1968) 412.

[18] A. Takuwa, Chem. Lett. (1989) 5.

[19] M.B. Rubin, Chem. Rev. 75 (1975) 177.