

## Photochemistry of Cyclic Vicinal Tricarbonyl Compounds. Photochemical Reaction of 1,2,3-Indanetrione with 2,3-Dimethyl-2-butene: Hydrogen Abstraction and Photocycloaddition

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A irradiação na região do ultravioleta de 1,2,3-indanotriona, em presença de 2,3-dimetil-2-buteno, em diclorometano, leva a uma mistura complexa de produtos formados a partir de reações de abstração de hidrogênio, fotocicloadição  $[2_{\pi}+2_{\pi}]$  (reação de Paternò-Büchi) e fotocicloadição  $[4_{\pi}+2_{\pi}]$ . A distribuição de produtos é dependente de fatores eletrônicos e estéricos, com estes últimos sendo os responsáveis pelo alto rendimento químico de formação do produto resultante da cicloadição fotoquímica  $[4_{\pi}+2_{\pi}]$ .

UV irradiation of 1,2,3-indanetrione, in  $\text{CH}_2\text{Cl}_2$ , in the presence of 2,3-dimethyl-2-butene yields a complex mixture of products arising from hydrogen abstraction,  $[2_{\pi}+2_{\pi}]$  photocycloaddition (Paternò-Büchi reaction), and  $[4_{\pi}+2_{\pi}]$  photocycloaddition. The reaction is dependent on electronic and steric effects, with the later accounting for the high chemical yield observed for the formation of the dioxene-type product.

**Keywords:** 1,2,3-Indanetrione, photochemistry, hydrogen abstraction, Paternò-Büchi

### Introduction

The photochemistry of 1,2,3-indanetrione (**1**) was examined by us in solution, at room temperature, by steady state and laser flash photolysis<sup>1</sup>. Its triplet state ( $E_T=42 \text{ kcal mol}^{-1}$ ,  $\tau=6,5 \text{ } \mu\text{s}$ ,  $\lambda_{\text{max}}=360 \text{ and } 570 \text{ nm}$ , in acetonitrile) preferentially reacts by a fast  $\alpha$ -cleavage process, followed by a considerably slower loss of carbon monoxide. Laser flash photolysis studies of **1** showed that in the presence of hydrogen donors, such as 1,4-cyclohexadiene or toluene, the triplet state of **1** decays with a rate constant of  $1,4 \times 10^6 \text{ mol}^{-1}\text{L s}^{-1}$ , leading to the formation of the ketyl radical 2-hydroxy-1,3-indandion-2-yl (**1a**). This quite fast rate constant is probably due to the extra stabilization of the ketyl radical by the vicinal and coplanar carbonyls to the radical center<sup>1,2</sup>.

Photolysis of 1,2,3-indanetrione under laser-jet conditions leads to the formation of 1,2-benzocyclobutenedione as the main product<sup>3</sup>.

Steady state UV irradiation ( $\lambda_{\text{exc}}=300 \text{ nm}$ ) of **1** in the presence of electron rich olefins with no allylic hydrogens such as 2,3-diphenyl-1,4-dioxene, leads to the formation of the corresponding oxetane **2**, through a  $[2\pi + 2\pi]$  photocycloaddition (Paternò-Büchi reaction) (Scheme 1, reaction A)<sup>4</sup>. On the other hand, photolysis of **1** with

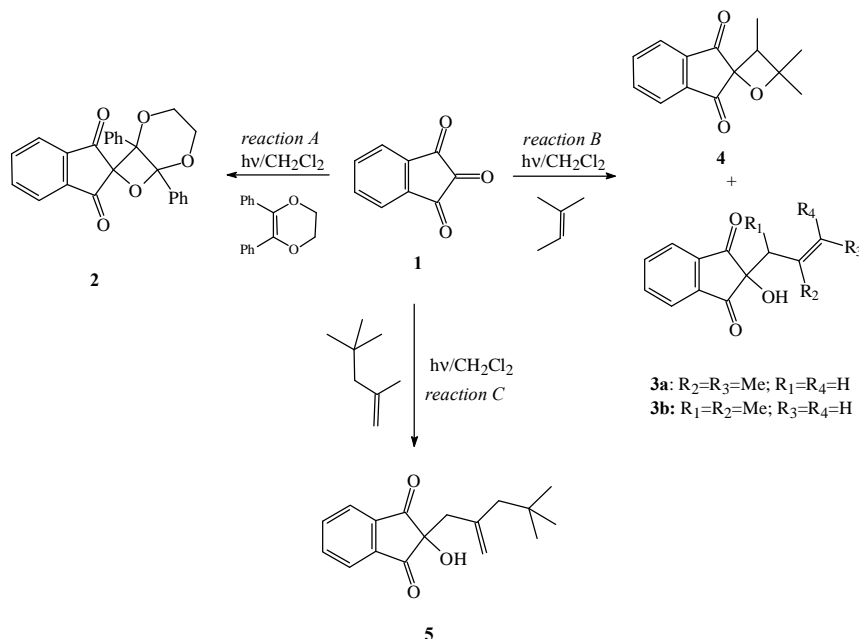
electron-rich olefins containing allylic hydrogens, such as 2-methyl-2-butene, results in the formation of products by hydrogen abstraction and  $[2\pi + 2\pi]$  photocycloaddition (Scheme 1, reaction B)<sup>4</sup>. For 1,1-di-substituted olefins containing allylic hydrogens, such as 2,4,4-trimethyl-1-pentene<sup>4</sup>, cyclohexene<sup>5</sup> and 2-methyl-1-butene<sup>5</sup>, the only observed product was that resulting from a hydrogen abstraction process. This is shown in Scheme 1 (reaction C), taking 2,4,4-trimethyl-1-pentene as a representative example.

In this paper we show that the photochemistry of 1,2,3-indanetrione **1** in the presence of 2,3-dimethyl-2-butene results in the formation of products derived from both hydrogen abstraction and photocycloaddition processes.

### Experimental

#### Materials

The solvents employed were Aldrich Spectrograde and were used as received. The olefin 2,3-dimethyl-2-butene was purchased from Aldrich. 1,2,3-Indanetrione (**1**) was synthesized by heating ninhydrin (Aldrich) in the presence of excess thionyl chloride under reflux<sup>6</sup> (mp 254-255°C; lit<sup>6</sup> 255°C). Alternatively, **1** was prepared by sublimative



Scheme 1.

dehydration of ninhydrin<sup>7</sup>, showing the same melting point, *ca.* 244-245°C. After preparation, the red-violet crystals were kept in sealed ampoules under reduced pressure.

#### General Techniques

GC analysis were carried out on a Varian model 2400 capillary gas chromatograph employing a 15 m T & W bonded phase vitreous silica FFAP column, under the following conditions:  $T_{\text{column}}$  from 50 to 200°C, at 40°C min<sup>-1</sup>;  $T_{\text{detector}}$ =300°C;  $T_{\text{injector}}$ =250°C. Gas chromatography-mass spectra (GC-MS) analysis were carried out on a Hewlett-Packard model 5970/5890 employing a 50 m J & L bonded phase vitreous silica HP-54 column. Mass spectra of main chromatogram peaks were obtained by electron impact with the spectrometer operating at 70 eV. Infrared spectra (IR) were obtained in a model 1420 Perkin-Elmer spectrophotometer in CCl<sub>4</sub> liquid film and using a NaCl cell. One- (1D) and two-dimensional [2D: homonuclear <sup>1</sup>H x <sup>1</sup>H-COSY and heteronuclear <sup>1</sup>H x <sup>13</sup>C-COSY-*n*J(CH) (n=1; n=2 and 3, COLOC)] <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded in a Bruker AC 200 spectrometer (<sup>1</sup>H: 200 MHz; <sup>13</sup>C: 50.3 MHz) in CDCl<sub>3</sub> using tetramethylsilane (TMS) as the internal standard.

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

#### Steady State Photolysis and Product Analysis

Irradiations were performed in a Rayonet with 9 RPR-3000 lamps ( $\lambda_{\text{exc}}$ =300 nm), at room temperature. Typical

samples were 100 mL of a 10<sup>-2</sup> mol L<sup>-1</sup> 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 olefin was irradiated until the green color of the original dichloromethane solution became pale yellow (less than one hour irradiation). The products were isolated by preparative thin-layer chromatography (silica, and chloroform:acetone 9:1 as eluent) and analyzed by IR, GC-MS, <sup>1</sup>H- and <sup>13</sup>C-NMR spectra. Chemical yields were based on isolated products.

Comparative analysis of <sup>13</sup>C NMR-HBBD (Hydrogen Broad Band Decoupled) and <sup>13</sup>C NMR-DEPT [Distortionless Enhancement by Polarization Transfer:  $\theta = 90^\circ$  (signal due to C-H only) and  $\theta = 135^\circ$  (CH and CH<sub>3</sub> signals in opposite phase to CH<sub>2</sub>)] spectra of **6a**, **b-8** allowed us to recognize the signals corresponding to methyl, methylene, methine and quaternary carbons (Table 1).

Unambiguous assignments of the chemical shifts of the hydrogen and carbon atoms of **6a**, **b-8** were obtained by heteronuclear 2D <sup>1</sup>Hx<sup>13</sup>C shift correlation via one bond [<sup>1</sup>H x <sup>13</sup>C-COSY-<sup>1</sup>J(CH) (Table 1)] and two <sup>2</sup>J(CH) and three <sup>3</sup>J(CH) [<sup>1</sup>H x <sup>13</sup>C-COSY-*n*J(CH) (n=2 and 3, COLOC),] spectra (Table 2).

#### 2-Hydroxy-2-[2',3'-dimethyl-2'-buten-1'-yl]-1,3-indanedione (**6a**)

IR  $\nu_{\text{max}}$  /cm<sup>-1</sup> 3422, 1716, 1601, 1590, 1450, 715; MS *m/z* 202 (20.1%), 176 (32.5%), 161 (10.3%), 160

**Table 1.**  $^1\text{H}$  (200 MHz) and  $^{13}\text{C}$  (50.3 MHz) NMR spectral data for **6a,b-8** in  $\text{CDCl}_3$  and TMS as internal standard\*.

	<b>6a</b>		<b>6b</b>		<b>7</b>		<b>8</b>	
	$d_{\text{C}}$	$d_{\text{H}}$	$d_{\text{C}}$	$d_{\text{H}}$	$d_{\text{C}}$	$d_{\text{H}}$	$d_{\text{C}}$	$d_{\text{H}}$
<b>C</b>								
1	200.02	-	199.63	-	202.63	-	185.74	-
2	78.84	-	81.32	-	89.22	-	139.82	-
3	200.02	-	199.63	-	202.63	-	154.93	-
8	140.52	-	141.57	-	a	-	129.12	-
9	140.52	-	141.57	-	a	-	135.89	-
1'	-	-	46.26	-	-	-	-	-
2'	120.14	-	147.31	-	90.50	-	79.35	-
3'	132.31	-	-	-	49.27	-	83.25	-
<b>CH</b>								
4	123.54	7.99-7.95	122.90	7.94-7.92	124.91/124.30	7.80-7.74	115.97	6.78 (d, 6.5)
5	136.29	7.89-7.86	136.02	7.86-7.83	136.71/136.90	7.80-7.74	132.17	7.11 (m)
6	136.29	7.89-7.86	136.02	7.86-7.83	136.71/136.90	7.80-7.74	128.15	6.98 (m)
7	123.54	7.99-7.95	122.90	7.94-7.92	124.91/124.30	7.80-7.74	120.73	7.11 (m)
<b>CH<sub>2</sub></b>								
1'	42.51	2.75 (s)	-	-	-	-	-	-
3'	-	-	115.56	4.83 (br s) 4.79 (br s)	-	-	-	-
<b>CH<sub>3</sub></b>								
4'	20.80	1.47 (s)	22.61	1.25 (s)	18.82	1.10 (s)	-	-
5'	20.34	1.43 (s)	22.61	1.25 (s)	22.70	0.64 (s)	21.43	1.26 (s)
6'	21.15	1.61 (s)	21.69	1.51 (s)	26.70	1.44 (s)	21.43	1.26 (s)
7'	-	-	-	-	23.92	1.01 (s)	23.37	1.32 (s)
8'	-	-	-	-	-	-	23.37	1.32 (s)

\*Chemical shifts ( $d_{\text{H}}$ , ppm) and multiplicity of hydrogen signals were obtained from 1D  $^1\text{H}$  NMR spectra; signals described without multiplicity were assigned with the aid of the heteronuclear  $^1\text{H} \times ^{13}\text{C}$ -COSY- $^nJ(\text{CH})$  ( $n=1; n=2$  and  $3$ , COLOC, Table 2) spectra. The homonuclear  $^1\text{H} \times ^1\text{H}$ -COSY and heteronuclear  $^1\text{H} \times ^{13}\text{C}$ -COSY- $^nJ(\text{CH})$  ( $n=1; n=2$  and  $3$ , COLOC, Table 2) spectra were also used for these assignments. Multiplicity of signals of carbon atoms deduced by comparative analysis of HBBB- and DEPT- $^{13}\text{C}$  NMR spectra.

<sup>a</sup>Chemical shifts not assigned due to small accumulation.

(83.9%), 159 (96.4%), 132 (8.9%), 131 (12.8%), 105 (15.2%), 104 (54.6%), 86 (50.7%), 83 (7.7%), 82 (100.0%), 77 (28.6%), 76 (70.3%), 67 (65.0%).

#### 2-Hydroxy-2-[1',1',2'-trimethyl-2'-propen-1'-yl]-1,3-indanedione (**6b**)

IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3449, 1710, 1631, 1590, 1450, 715; MS  $m/z$  244 ( $[\text{M}]^+$ , 1.0%), 229 (4.3%), 162 (100.0%), 133 (11.2%), 132 (11.3%), 105 (19.8%), 104 (61.9%), 83 (90.0%), 77 (27.8%), 76 (51.3%), 69 (20.9%).

#### 2-Spiro-2'-[2',2',3',3'-tetramethyloxetane]-1,3-indanedione (**7**)

IR  $\nu_{\text{max}}/\text{cm}^{-1}$  1776, 1710, 1590, 1450, 1260, 950, 715; MS  $m/z$  244 ( $[\text{M}]^+$ , 34.0%), 229 (70.3%), 204 (25.90%), 189 (95.9%), 162 (11.7%), 161 (100.0%), 133 (10.2%), 132 (36.8%), 105 (52.9%), 104 (52.5%), 84 (49.6%), 77 (43.8%), 76 (31.4%), 69 (38.8%).

#### 2,3-[2',2',3',3'-tetramethyl-1',4'-dioxene]-inden-1-one (**8**)

IR  $\nu_{\text{max}}/\text{cm}^{-1}$  1712, 1644, 1590, 1450, 1037, 919, 715; MS  $m/z$  244 ( $[\text{M}]^+$ , 23.2%), 162 (25.5%), 104 (18.5%), 84 (80.6%), 76 (22.9%), 69 (100.0%).

## Results and Discussion

Photolysis of **1** ( $\lambda = 300$  nm) in the presence 2,3-dimethyl-2-butene leads to a complex mixture of products derived from a hydrogen abstraction process, *i.e.* **6a** (5.7%) and **6b** (11.8%), a  $[2_{\pi}+2_{\pi}]$  photocycloaddition reaction, the oxetane **7** (29.4%), and a  $[4_{\pi}+2_{\pi}]$  photocycloaddition reaction, the 2,3-[2',2',3',3'-tetramethyl-1',4'-dioxene]-inden-1-one (**8**) (53.1%) (Scheme 2).

The photochemistry of vicinal triketoones has great similarity to that described for monoketoones. The reaction with electron donors leads to the formation of the corresponding anion radical<sup>9</sup>, whereas in the presence of hydrogen donors the ketyl radical is usually observed<sup>4</sup>. For the case of 1,2,3-indanetrione (**1**), its photochemical behavior involves a triplet excited state of  $n\pi^*$  character and very low energy<sup>4,10</sup>.

It has recently been shown that photolysis of **1** in the presence of olefins is controlled by substitution at the double bond<sup>4</sup>. Dialkyl-substituted olefins containing allylic hydrogens yield only hydrogen abstraction products, whereas trialkyl-substituted olefins are able to form products arising from hydrogen abstraction and photocycloaddition processes. Furthermore, electronic and steric effects seem to play a very

**Table 2.** Heteronuclear long-range coupling via two ( $^2J_{\text{CH}}$ ) and three ( $^3J_{\text{CH}}$ ) bonds observed in the  $^1\text{H}\times^{13}\text{C}$ -COSY- $^nJ_{\text{CH}}$  ( $n=2$  and  $3$ , COLOC) spectra of **6a**, **6b**, **7**, and **8**, in  $\text{CDCl}_3$ .\*

	<b>6a</b>		<b>6b</b>		<b>7</b>		<b>8</b>	
	$^2J(\text{CH})$	$^3J(\text{CH})$	$^2J(\text{CH})$	$^3J(\text{CH})$	$^2J(\text{CH})$	$^3J(\text{CH})$	$^2J(\text{CH})$	$^3J(\text{CH})$
<b>C</b>								
1		H-4 H-7 2H-1'		H-4 H-7				
2	2H-1'			3H-4' 3H-5'		3H-4' 3H-5'		
3		H-4 H-7 2H-1'		H-4 H-7				H-4
8	H-7	H-4 H-6	H-7	H-4 H-6				H-4 H-6
9	H-4	H-5 H-7	H-4	H-5 H-7				H-5 H-7
1'	-	-	3H-4' 3H-5'	2H-3'				
2'	3H-5' 2H-1'	3H-4' 3H-6'	3H-6'	3H-4' 3H-5'	3H-6' 3H-7'	3H-4' 3H-5'	3H-7' 3H-8'	3H-5' 3H-6'
3'	3H-4' 3H-6'	2H-1' 3H-5'			3H-4' 3H-5'	3H-6' 3H-7'	3H-5' 3H-6'	3H-7' 3H-8'
<b>CH</b>								
4	H-5							H-6
5	H-4							H-7
6	H-7							H-4
7	H-6							H-5
<b>CH<sub>2</sub></b>								
1'		3H-5'	-	-				
3'	-	-		3H-6'				
<b>CH<sub>3</sub></b>								
4'		3H-6'				3H-5'		
5'		2H-1'				3H-4'		
6'		3H-4'		2H-3'		3H-7'		
7'	-	-				3H-6'		
8'	-	-						

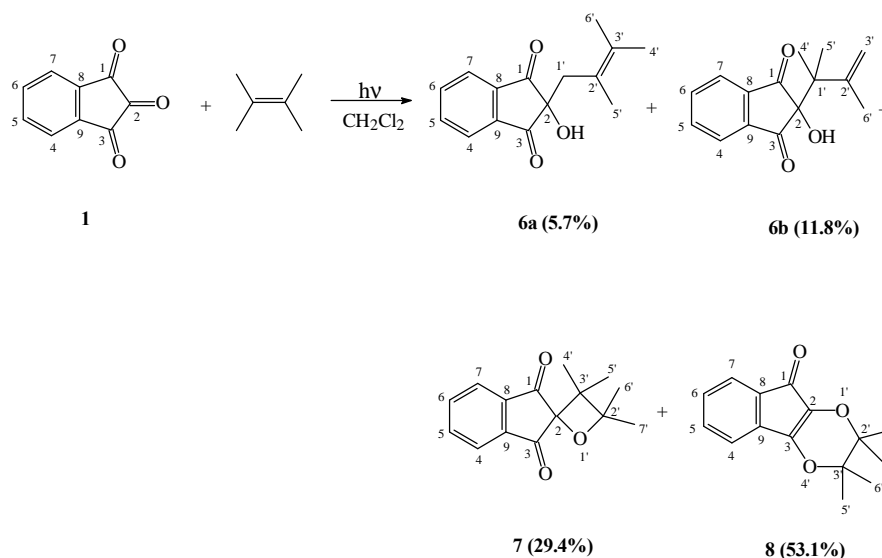
\*  $^1\text{H}\times^1\text{H}$ -HOMOCOSY and  $^1\text{H}\times^{13}\text{C}$ -HETCOSY- $^1J(\text{CH})$  (Table 1) spectra were also used in these analysis.

important role in the photochemical reaction of this triketone in the presence of alkenes. Thus, photolysis of **1** and electron-rich olefins containing no allylic hydrogens yields oxetanes with quantum yields close to unity. However, no reaction was observed when the irradiation was performed in the presence of olefins substituted by electron-acceptor groups<sup>4</sup>.

The  $n\pi^*$  excited state of the tricarbonyl can be quenched by di-substituted olefins containing no allylic hydrogens without product formation. For example, when 1,2,3-indanetrione is photolyzed in the presence of diastereoisomerically pure *cis*- or *trans*-stilbene, in which direct energy transfer from the triketone to the olefin is not possible due to the endothermicity of the process, olefin isomerization could be observed. Moreover, the same *cis/trans* ratio was obtained independently of the configuration of the starting isomer. This is fully in accord with the involvement of an exciplex on the quenching process<sup>11-13</sup>.

Quenching rate constants by olefins are much larger than those for the formation of either a 1,4-biradical or a radical pair and this precludes the direct formation of any of these two species. Furthermore, product formation in the photolysis of **1** with some olefins, such as 2,4,4-trimethyl-1-pentene and 2-methyl-2-butene, does not involve the most stable 1,4-biradical (in photocycloaddition) or allylic radical (in hydrogen abstraction). These results seem to confirm the involvement of an exciplex as the precursor for the 1,4-biradical or the radical pair in the photolysis of 1,2,3-indanetrione and 2,3-dimethyl-2-butene, with this exciplex being directly formed from the triplet excited state of the triketone<sup>14</sup>.

Thus, the reaction of **1** in the presence of alkenes can mechanistically be explained by a primary interaction between triplet 1,2,3-indanetrione and the olefin, forming an exciplex with some charge-transfer character<sup>11-13</sup>, in



Scheme 2.

which the olefin is the donor and the triketone the acceptor. Since in the triketone-olefin pair the topological nature of the potential surface for the formation of cycloaddition products is the same as for hydrogen abstraction, the exciplex responsible for both processes is probably the same<sup>15,16</sup>. This exciplex then decays to a radical pair (for hydrogen abstraction), or a 1,4-biradical (for cycloaddition), intermediates responsible for product formation<sup>4</sup>.

The primary process involved in the formation of products **6a** and **6b** is an allylic hydrogen abstraction from the olefin. Since all 12 hydrogens of 2,3-dimethyl-2-butene are equivalent, the hydrogen abstraction leads to only one primary and allylic radical. This initially formed radical has a more stable resonance form in which the carbon centered radical is allylic but located in a tertiary carbon. The higher stability of this resonance form would explain the difference in the chemical yield between **6a** (5.7%) and **6b** (11.8%).

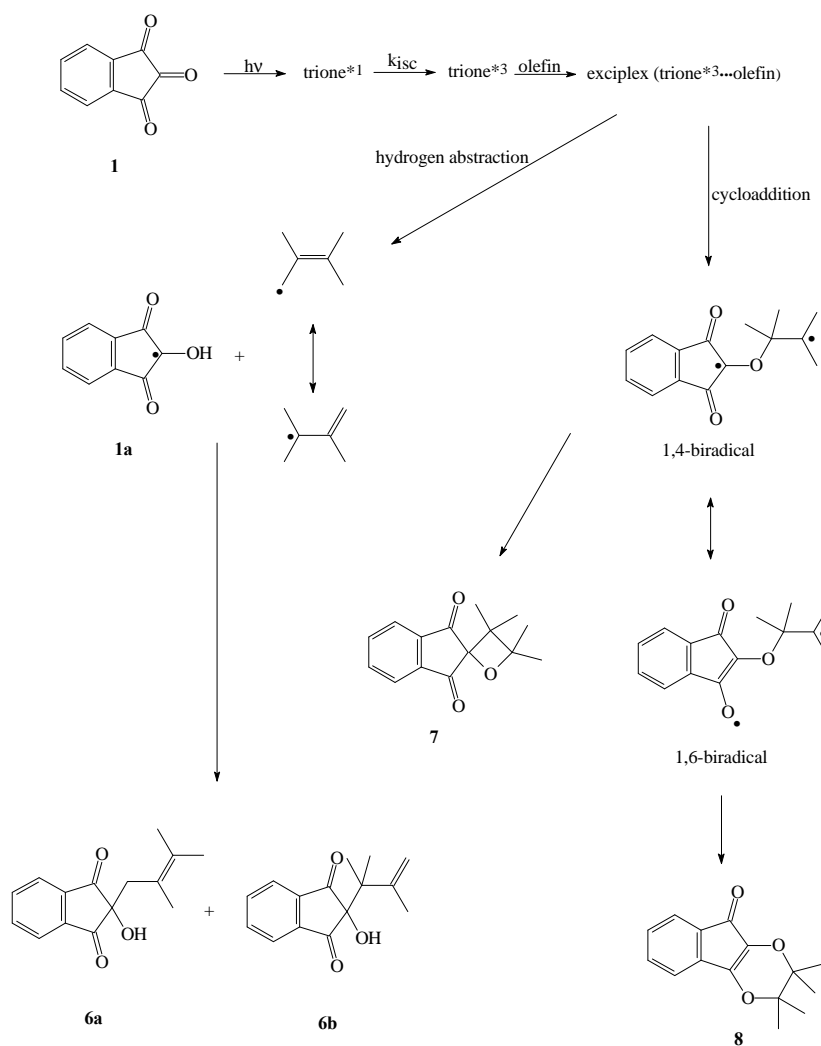
Electronic and steric factors are clearly present in the reaction between **1** and 2,3-dimethyl-2-butene. The tetra-substitution on the olefin double bond makes it an electron-rich species and, therefore, capable of yielding products resulting from the attack of the  $n\pi^*$  electron-deficient oxygen of the triketone to the double bond. In this case, the product resulting from an initially formed 1,4-biradical can be observed, *i.e.* the oxetane **7**. The lower chemical yield obtained in the formation of **7** (29.4%), when compared to **8** (53.1%), can be explained by a strong steric effect caused by the presence of the four methyl groups. The tetra-substitution on the already strained four-member ring of the oxetane moiety would be responsible for a further increase in the steric hindrance experienced by this species. Then, it is not surprising that in this case the formation of **8**, product arising from a 1,6-biradical, was observed. But even with

such strong steric effect, it is important to note that the formation of cycloaddition products accounts for more than 80 % of total products. This clearly indicates a preference for the formation of the 1,4-biradical in detriment of the radical pair resulting from the hydrogen abstraction process. Steric effects in the reaction of **1** with olefins are present not only on the transition state for product formation, but also on the approximation between the excited ketone and the olefin. This was recently demonstrated in the reaction of 1,2,3-indanetrione with 2,4,4-trimethyl-1-pentene or 2-methyl-2-butene.<sup>4</sup> In both cases no evidence was found for the abstraction of the allylic hydrogen leading to the more stable radical.

A clear trend on the reactivity of triplet **1** with olefins containing allylic hydrogen emerges from these and previous results.<sup>4</sup> While di-substituted olefins, such as cyclohexene<sup>5</sup> or 2,4,4-trimethyl-1-pentene<sup>4</sup>, give only hydrogen abstraction products, the tri-substituted olefin 2-methyl-2-butene form a mixture of hydrogen abstraction products and oxetane, with the later being a minor product. With tetra-substituted olefins there is a large preferential formation for photocycloaddition products (Table 3). This clearly indicates that electronic effects mainly control the photocycloaddition.

**Table 3.** Chemical yields for product formation as a function of olefin substitution.

Olefin	Hydrogen abstraction	Photocycloaddition	Ref.
	(%)	(%)	
cyclohexene	100	-	5
2,4,4-trimethyl-1-pentene	100	-	4
2-methyl-2-butene	82.0	18.0	4
2,3-dimethyl-2-butene	17.5	82.5	this work



Scheme 3.

Based on the above discussion, Scheme 3 shows a detailed mechanism for the formation of products **6a**, **6b**-**8** from the reaction between **1** triplet and 2,3-dimethyl-2-butene.

## Conclusion

In conclusion, it was shown that the photochemical reaction between **1** and 2,3-dimethyl-2-butene is dependent on electronic and steric effects. Thus, products derived from the 1,4-biradical, formed by the attack of the  $\pi^*$  electron-deficient oxygen of the triketone to the highly substituted double bond of the olefin, are preferentially formed. On the other hand, steric effects on the formation of the oxetane **7** account for the high chemical yield of dioxene **8**. This type of product is being observed for the first time on the photochemistry of cyclic vicinal tricarbonyl compounds.

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