198. Photochemistry of Ethyl 2,3-Dihydro-2,2-dimethyl-3-oxo-1*H*-pyrrole-1-carboxylate

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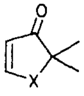
Dedicated to Prof. Dr. *W. Walter* on the occasion of his 70th birthday

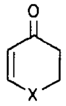
(15.IX.89)

The title compound **7** is obtained by reductive dehalogenation from 4-bromo-2,3-dihydro-2,2,-dimethyl-3-oxo-1*H*-pyrrole-1-carboxylate (**8**) in 90% yield. Aza-enone **7** undergoes [2 + 2] cycloaddition from the triplet state with both electron-rich and electron-deficient alkenes. The behaviour of **7** in light-induced reactions is compared to those of 2,2-dimethyl-3(2*H*)-furanone (**1a**) and of the corresponding thiophenone **1b**. In the photodimerization and the cycloaddition to either 2,3-dimethylbut-2-ene or to dimethyl maleate of these ketonic five-membered heterocycles with one heteroatom, the overall efficiency increases in going from the furan **1a** to the thiophene **1b** and to the pyrrole **7**.

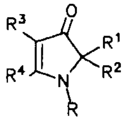
Introduction. – Intermolecular [2 + 2] photocycloadditions of cyclic α,β-unsaturated ketones to alkenes represent one of the most important light-induced reactions in organic synthesis [1–4]. In addition to cyclopent-2-enones and cyclohex-2-enones, five- and six-membered heterocyclic enones, *e.g.* **1** and **2**, have often been used as starting compounds. Among those the O-heterocycles **1a** and **2a** have been studied intensively [5] [6] and the corresponding S-compounds **1b** and **2b** occasionally [7] [8].



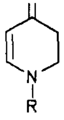
1a X = O
b X = S



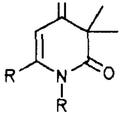
2a X = O
b X = S



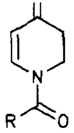
3a $R^3 = R^4 = CH_3$, $R = R^1 = R^2 = H$
b $R^1 = R^2 = CH_3$, $R = R^3 = R^4 = H$
c $R = (CH_3)_2CH$, $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$
d $R^1 = CH_3$, $R^2 = CO_2CH_3$, $R = R^3 = R^4 = H$
e $R^1 = CH_2CHCH_2$, $R^2 = CO_2CH_3$, $R = R^3 = R^4 = H$



4a $R = CH_3$
b $R = CH_2C_6H_5$
c $R = CH(C_6H_5)_2$



5 R = H, CH_3

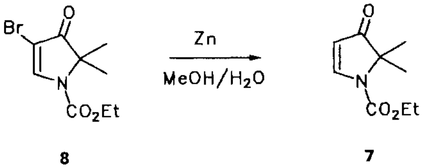


6a $R = C_6H_5$
b $R = OCH_3$

The behaviour of aza-enones is more complex. In the five-membered ring series (compounds **3**), it has been found that none of the 3-oxopyrroles **3a** [9], **3b** [10], **3c** [7], **3d** [11], and **3e** [12] undergoes [2 + 2] photocycloadditions to alkenes, neither on direct nor on acetone-sensitized irradiations. It has been proposed [7] that compounds **3** undergo efficient self quenching *via* electron transfer between a ground- and an excited-state molecule followed by electron back-transfer between the two ion radicals. Similarly six-membered aza-enones **4**, *e.g.* the *N*-alkyl-2,3-dihydropyridin-4-(1*H*)-ones **4a–c** do not react with alkenes on direct irradiation to give cyclobutanes. Nevertheless, these compounds undergo inefficient cycloaddition to dimethyl maleate in acetone-sensitized reactions, although it is not evident, if the triplet energy is transferred to **4** or the unsaturated ester [13]. In contrast, vinylogous imides, *e.g.* **5** [14] or **6a** [15], the vinylogous *N*-acylcarbamate **6b** [16], and pyrimidinediones as uracil [17] photodimerize and undergo [2 + 2] cycloadditions to alkenes, mostly in acetone-sensitized reactions. We now report on the synthesis of the five-membered 3-oxopyrrole-1-carboxylate **7a** and on comparative results of its photochemical behaviour to that of furanone **1a** and thiophenone **1b**.

Results. – As we had met with difficulties in trying to obtain **7** by dehydrobromination of ethyl 4-bromo-2,2-dimethyl-3-oxopyrrolidine-1-carboxylate [10], we thought of ethyl 4-bromo-2,3-dihydro-2,2-dimethyl-3-oxo-1*H*-pyrrole-1-carboxylate (**8**), readily available from methylalanine in four steps in 26% overall yield [10], as precursor of **7**. Indeed, reductive dehalogenation of **8** with either Zn or Cu, or light-induced in i-PrOH, affords **7**, the best yield (90%) being obtained with Zn in MeOH/H_2O 10:3 *(Scheme 1)*.

Scheme 1



On photolysis (λ = 350 nm) in MeCN, **7** affords a single photodimer **9** whose constitution (head-to-head) and configuration *(cis-transoid-cis)* is deduced from the ^{1}H-NMR coupling constants and from the fact that **9** is resolved into enantiomers by GLC on a chiral stationary phase [18] *(Scheme 2)*. Only one regioisomer **10a** is formed in the presence of 2-methylpropene and again only the two diastereoisomeric cyclobutanes **10b** and **10c** in the presence of 2-methoxypropene. Irradiation of **7** and 2,3-dimethylbut-2-ene affords hexamethylcyclobuta[*b*]pyrrolecarboxylate **11** quantitatively. Finally, irradiation of **7** in the presence of either (*Z*)- or (*E*)-but-2-ene yields identical diastereoisomeric 2:1:5 mixtures **12a**/**12b**/**12c**, and similarly with either dimethyl maleate or dimethyl fumarate, identical 1:1 mixtures **13a**/**13b** are formed *(Scheme 2)*. The spectroscopic data of photoproducts **9–13** is summarized in *Table 1*.

These results indicate that **7** exhibits a very similar photoreactivity to both **1a** [5] and **1b** [7]. As the reaction of these two latter enones with dimethyl maleate or fumarate had not been investigated before, we have irradiated **1a** and **1b** in the presence of these

Scheme 2

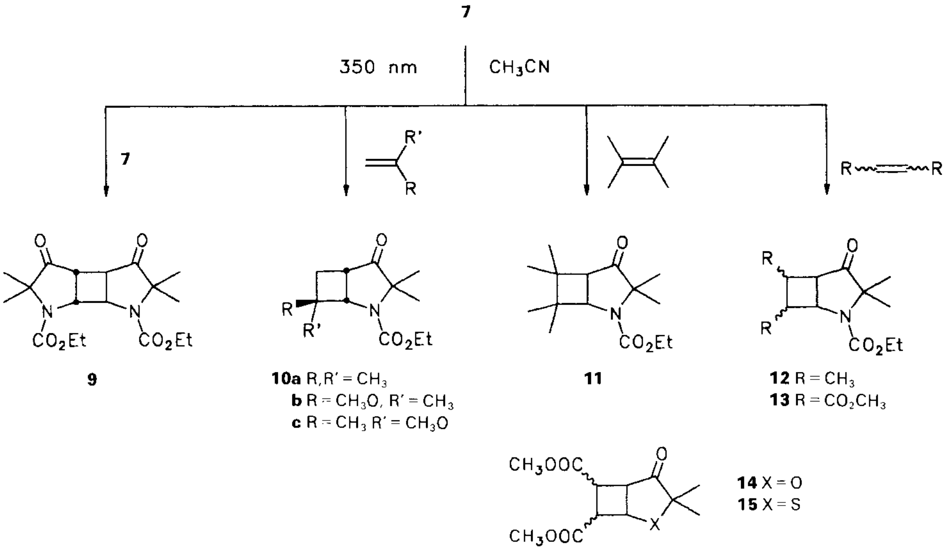


Table 1. *Spectroscopic Data of Perhydrocyclobuta[*b*]pyrrolcarboxylates* **9–13**

	IR[a])	^{1}H-NMR[b])[c])	^{13}C-NMR[d])	CI-MS
9	1748	4.00, 2.52 (*AA'XX*, $J_{AA'} = 3.0$, $J_{AX'} = 7.4$, $J_{AX'} = -1{,}8$, $J_{XX'} = 0$)	212 (*s*); 156 (*s*); 65 (*s*); 61 (*t*); 43 (*d*); 30 (*d*); 25, 24, 14 (*q*)	367 (3, *M*H$^+$), 184 (100)
10a	1750 1710	3.78 (*d*, *J* = 7.8); 2.63 (*ddd*, *J* = 5.4, 7.8, 10.8); 1.66 (*dd*, *J* = 10.4, 12.0); 1.55 (*dd*, *J* = 5.4, 12.0)	216 (*s*); 154 (*s*); 66 (*s*); 61 (*d*); 60 (*t*); 40 (*d*); 37 (*s*); 36 (*t*); 28, 24, 23, 22, 14 (*q*)	240 (9, *M*H$^+$), 184 (100)
10b	1750 1700	4.19 (*d*, *J* = 8,0); 2.49 (*ddd*, *J* = 4.0, 8.0, 9.8); 1.89 (*dd*, *J* = 4.0, 12.8); 1.51 (*dd*, *J* = 9.8, 12.8)		256 (100, *M*H$^+$)
10c	1750 1700	3.85 (*d*, *J* = 8,0); 2.48 (*ddd*, *J* = 4.0, 8.0, 9.8); 1.90 (*dd*, *J* = 4.0, 12.8); 1.52 (*dd*, *J* = 9.8, 12.8)		256 (100, *M*H$^+$)
11	1745 1719	3.76 (*d*, *J* = 8.6); 2.35 (*d*, *J* = 8.6)	215 (*s*); 155 (*s*); 67 (*s*); 61 (*t*); 60 (*d*); 50 (*s*); 43 (*d*); 40 (*s*); 27, 24, 23, 22, 21, 20, 14 (*q*)	268 (100, *M*H$^+$)
12a–c	1750 1700			240 (100, *M*H$^+$)
13a[d])[e])	1750 1734	4.78 (*dd*, *J* = 6.6, 7,6); 4.06 (*dd*, *J* = 6.2, 6.6); 3.65 (*dd*, *J* = 5.0, 6.2); 3.36 (*dd*, *J* = 5.0, 7.6)		237 (5, *M*$^+$), 110 (100)

Table 1 (cont.)

	IR[a])	^{1}H-NMR[b])[c])	^{13}C-NMR[d])	CI-MS
13b[d])[e])	1750 1734	4.61 (*dd, J* = 5.0, 7,6); 4.03 (*dd, J* = 6.2, 7.2); 3.73 (*dd, J* = 5.0, 7.2); 3.34 (*dd, J* = 6.2, 7.6)		237 (5, M^+), 110 (100)

[a]) In CCl_4. [b]) Only cyclobutane C*H* given. [c]) In $CDCl_3$. [d]) ^{1}H-NMR in CD_3COCD_3. [e]) EI-MS at 70eV.

unsaturated esters. As now expected, both compounds again afford identical product mixtures when starting with either the (*Z*)- or the (*E*)-ester (**14a–c** 5:2:1 for **1a** and **15a–c** 2:5:1 for **1b**).

We next compared the overall rate of conversion of **7**, **1a**, and **1b** ($3 \cdot 10^{-4}$ M) in MeCN to cycloadducts in the absence of alkenes (photodimerization) and in the presence of a 100-fold molar excess of either 2,3-dimethylbut-2-ene or dimethyl maleate. From these relative rates summarized in *Table 2*, it can be seen that **7** reacts more efficiently than either **1a** or **1b** in the three types of cycloadditions studied.

Table 2. *Relative Rates of Conversion of* **1a**, **1b**, and **7** ($3 \cdot 10^{-4}$ M in MeCN) *to Cycloadducts.* Irradiation with $\lambda > 300$ nm.

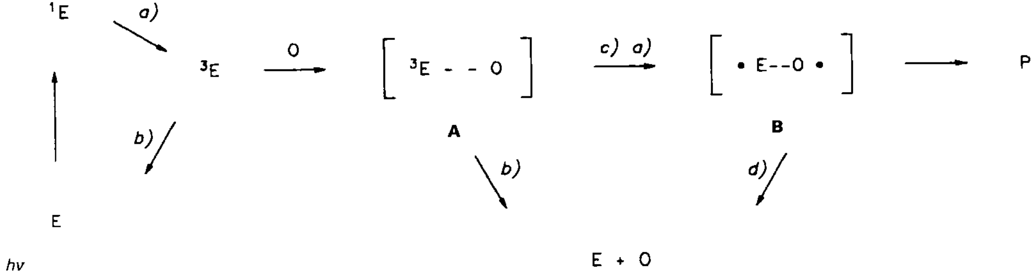
Conditions	Relative rates		
	1a	**1b**	**7**
In absence of alkenes	0.15	0.27	1.0
2,3-Dimethylbut-2-ene ($3 \cdot 10^{-2}$ M)	0.06	0.11	1.0
Dimethyl maleate ($3 \cdot 10^{-2}$ M)	0.04	0.07	0.44

Finally, we tried to determine the values of the triplet energies of **7**, **1a**, and **1b** by running the same three cycloadditions in MeCN in the presence of sensitizers (indanone, xanthone, benzophenone, thioxanthone) or quenchers (naphthalene). While the reactions of furanone **1a** are only sensitized by indanone, both **7** and **1b** form cycloadducts in the presence of each of the sensitizers used, although with thioxanthone the reactions of **1b** become much slower than those of **7**. These results and the fact that the reactions of all three enones are quenched efficiently by naphthalene suggests values E_T = 73–75 kcal/mol for **1a**, 63–65 kcal/mol for **1b**, and 62–63 kcal/mol for **7** [19]. From the *Stern-Volmer* plots, values of $k_q \cdot \tau$ = 24 M^{-1} (**7**), 42 M^{-1} (**1a**), and 71 M^{-1} (**1b**) are obtained, respectively. Assuming $k_q = 10^{10}$ $M^{-1} \cdot s^{-1}$ (*i.e.* the rate constant for diffusion in MeCN), one obtaines values of $\tau = 10^{-9}$–10^{-8} s for the corresponding lifetimes.

Discussion. – The results obtained in the photochemical experiments with the title compound **7** clearly demonstrate that five-membered aza-enones behave like their oxa and thia counterparts, *i.e.* after excitation they undergo spin inversion and react from the triplet state with alkenes to give [2 + 2] cycloadducts as does cyclopent-2-enone, but only if the N-atom bears a (electron-withdrawing) C=O group, *i.e.* the molecule becomes a less efficient electron donor.

Furthermore, several aspects regarding the generally accepted mechanism for enone cycloadditions [5] [20] [21] *(Scheme 3)* are worthwile mentionning. The question, if triplet exciplexes **4** are involved in such cycloadditions, has been raised [22], and the orientation

Scheme 3. *Formation of [2 + 2] Photocycloadducts (*P*) from Triplet Enone (*E*) and Olefin (*O*)* via *Exciplex* **A** *and Singlet Biradical* **B**



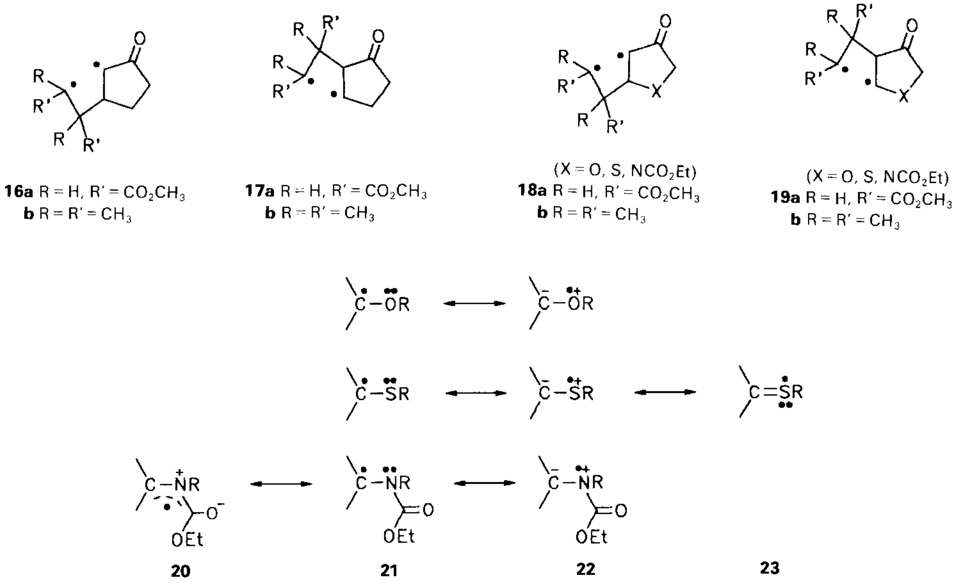
a) Intersystem crossing. b) Deactivation. c) C–C bond formation. d) Reversion.

of addition observed with 1,1-disubstituted ethylenes, *e.g.* the specific formation of products **10** from **7** and 2-methylpropene or 2-methoxypropene, analogously observed for **1a** and **1b**, *and* the specific formation of the opposite regioisomer in additions to 3-chloro-2-(chlorodifluoromethyl)-3,3-difluoropropene [5] [23] are the best evidence for an affirmative answer. In addition, very recently, good evidence for the existence of such exciplexes in *intramolecular* cycloadditions has also been advanced [24].

An interesting aspect of our results is the fact that all three hetero-enones **1a**, **1b**, and **7** undergo efficient cycloadditions to the electron-deficient alkenes, dimethyl maleate, and dimethyl fumarate, as the parent triplet cyclopent-2-enone is known to be intercepted by fumaronitrile more efficiently than by 2,3-dimethylbut-2-ene, but the quantum efficiency of (cyclobutane) product formation is zero with the (electron-deficient) unsaturated dinitrile and very high with the (electron-rich) alkene. It is, thus, necessary to explain why the overall reaction of cyclopent-2-enone with electron-deficient alkenes is so inefficient and why the hetero-enones **1a**, **1b**, and **7** afford products efficiently with *both* types of alkenes.

In the reaction of cyclopent-2-enone with 1,2-equally-substituted alkenes, two possible biradicals **16** and **17** can be formed. Independently of the fact that **16** is more stable than **17** by *ca.* 10 kcal/mol [25], for both **16a** and **17a**, the reversion to enone and alkene will be a much more favourable process than for **16b** and **17b** due to the important differences in enthalpies of formation of the olefins (–94 kcal/mol for the unsaturated ester *vs.* –18 kcal/mol for the alkene). Therefore, it can be assumed that both **16a** and **17a** will almost quantitatively revert to starting materials. Under the same conditions, hetero-enones **1a**, **1b**, and **7** will afford biradicals **18** and **19**. While the heteroatom does not contribute to the stability or **18** as compared to **16**, biradical **19** will be stabilized in comparison to **17** by interaction of one unpaired electron and the lone pair of the heteroatom, and this effect will increase in going from X = O to X = S and then to X = NCO_2Et due to better delocalization as shown in substructures **20**–**23** *(Scheme 4)*. Although *a priori* the higher stability – and, therefore, the longer lifetime – of an intermediate 1,4-biradical only implies that it will statistically adopt more often *both* conformations, the one required for ring closure and the other one required for cleavage of the central bond, the good correlation of increasing efficiency of cyclobutane formation with the increasing stabilization of biradical **19** with the varying heteroatoms seems to indicate, that at least in the reaction of **1a**, **1b**, or **7** with both dimethyl maleate or

Scheme 4



16a R = H, R' = CO$_2$CH$_3$
b R = R' = CH$_3$

17a R = H, R' = CO$_2$CH$_3$
b R = R' = CH$_3$

18a R = H, R' = CO$_2$CH$_3$
b R = R' = CH$_3$

19a R = H, R' = CO$_2$CH$_3$
b R = R' = CH$_3$

20 **21** **22** **23**

fumarate on the one side and 2,3-dimethylbut-2-ene on ther other side, the most stable biradical gives the highest yield of [2 + 2] cycloadducts.

Experimental Part

General. Qual. GC: 30-m *SE 30* capillary column. Prep. GC: 2-m 10% QF 1 on *Chromosorb W-AW DMCS* column. UV Spectra: in nm (log ε). IR Spectra: in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: at 400 MHz and 100.63 MHz, resp.; chemical shifts in ppm rel. to TMS (= 0 ppm). MS: at 70 eV.

Photolyses. Rayonet RPR 100 photoreactor equipped with 300-nm (*A*) or 350-nm lamps (*B*) or in an *Applied Photophysics* quantum-yield reactor using light of λ > 300 nm (*C*).

Starting Materials. Enones **1a** [26] and **1b** [7] were synthesized according to the literature procedures.

*Ethyl 2,3-Dihydro-2,2-dimethyl-3-oxo-1*H*-pyrrole-1-carboxylate* (**7**). To a suspension of Zn powder (7.5 g, 0.115 mol) in MeOH (200 ml) and H$_2$O (60 ml) was added ethyl *4-bromo-2,3-dihydro-2,2-dimethyl-3-oxo-1*H*-pyrrole-1-carboxylate* [10] (**8**; 8.25 g, 0.02 mol), and the mixture was refluxed for 2 h. After filtration from ZnBr$_2$ and evaporation, the residue was dissolved in CH$_2$Cl$_2$ and dried (MgSO$_4$). Distillation afforded 3.29 g (90%) of **7**, B.p. 120°/0.1 Torr. UV (MeCN): 286 (3.78). IR (film): 3075, 1725, 1680, 1580. ^{1}H-NMR (CDCl$_3$): 8.42 (*d*, *J* = 4.0, 1 H); 5.75 (*d*, *J* = 4.0, 1 H); 4.28 (*q*, 2 H); 1.41 (*s*, 6 H); 1.21 (*t*, 3 H). ^{13}C-NMR (CDCl$_3$): 204 (*s*); 156 (*d*); 148 (*s*); 105 (*d*); 65 (*s*); 62 (*t*); 21 (*q*); 14 (*q*). MS: 183 (42, *M*$^+$), 110 (100).

Preparative Irradiations of **7**. Ar-degassed solns. of **7** (732 mg, 4 · 10^{-3} mol) were irradiated (*B*) in MeCN (5 ml): *diethyl perhydro-2,2,5,5-tetramethyl-3,4-dioxo-*cis*-3a-*transoid*-3a,3b-*cis*-3b-cyclobuta[1,2-*b*:3,4-*b*]dipyrrole-1,6-dicarboxylate* (**9**). After 24 h, evaporation and chromatography (SiO$_2$, CH$_2$Cl$_2$/MeOH 19:1), 534 mg (73%) of **9** were obtained as colourless oil.

*Ethyl Perhydro-2,2,5,5-tetramethyl-3-oxo-*cis*-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate* (**10a**). A soln. saturated with 2-methylpropene was irradiated for 16 h. After evaporation, the residue was purified by bulb-to-bulb distillation (170°/0.02 Torr) to afford 755 mg (79%) of **10a** as colourless oil.

*Ethyl (3a*RS,*5*SR,*5a*RS*)- and (3a*RS,*5*RS,*5a*RS*)-Perhydro-5-methoxy-2,2,5-trimethyl-3-oxo-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate* (**10b** and **10c**, resp.). A soln. containing 2-methoxypropene (720 mg, 10 mmol) was irradiated for 16 h. Workup as described for **10a** afforded 877 mg (86%) of a 2:1 mixture of **10b**/**10c**; **10b**: MeO presumably *trans* to N.

*Ethyl Perhydro-2,2,4,4,5,5-hexamethyl-3-oxo-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate* (**11**). A soln. containing 2,3-dimethylbut-2-ene (840 mg, 10 mmol) was irradiated for 14 h. Bulb-to-bulb distillation (170°/0.02 Torr) afforded 961 mg (90%) of **11** as colourless oil.

*Ethyl Perhydro-2,2,4,5-tetramethyl-3-oxo-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate* (**12**). A soln. containing (*Z*)- or (*E*)-but-2-ene (50 mg, 10 mmol) was irradiated for 16 h. Bulb-to-bulb distillation affords 745 mg (78%) of a 2:1:5 mixture of **12a**/**12b**/**12c**. The rel. configurations of these diastereoisomers could not be derived from the ^{1}H-NMR data.

*1-Ethyl 4,5-Dimethyl Perhydro-2,2-dimethyl-3-oxo-1*H*-cyclobuta[*b*]pyrrole-1,4,5-tricarboxylate* (**13**). A soln. containing either dimethyl maleate or fumarate (720 mg, 5 mmol) was irradiated for 20 h. Bulb-to-bulb distillation (185°/0.02 Torr) afforded 1033 mg (79%) of a 1:1 mixture **13a**/**13b**. The rel. configurations of the diastereoisomers could not be derived from the ^{1}H-NMR data.

*Dimethyl Perhydro-2,2-dimethyl-3-oxocyclobuta[*b*]furan-4,5-dicarboxylate* (**14**). A soln. of **1a** (448 mg, 4 mmol) and dimethyl maleate (720 mg, 5 mmol) in MeCN (5 ml) was irradiated for 32 h. Bulb-to-bulb distillation (170°/0.02 Torr) afforded 932 mg (91%) of a 5:2:1 mixture **14a**/**14b**/**14c**. ^{1}H-NMR (C_6D_6, only H of cyclobutane): **14a**: 5.31 (*dd*, J = 5.0, 6.0); 3.80 (*dd*, J = 6.8, 7.6); 3.45 (*dd*, J = 6.0, 7.6); 2.93 (*dd*, J = 5.0, 6.8); **14b**: 4.48 (*dd*, J = 4.0, 4.6); 3.75 (*ddd*, J = 1.4, 4.0, 8.0); 3.42 (*dd*, J = 8.0, 10.4); 2,79 (*ddd*, J = 1.4, 6.4, 10.4). The rel. configurations could not be derived from this data. CI-MS: 257 (15, MH^+), 113 (100).

*Dimethyl Perhydro-2,2-dimethyl-3-oxocyclobuta[*b*]thiophene-4,5-dicarboxylate* (**15**). As described above, from **1b** (512 mg, 4 mmol) and dimethyl maleate (720 mg, 5 mmol), one obtained 870 mg (80%) of a 2:5:1 mixture **15a**/**15b**/**15c**. ^{1}H-NMR (C_6D_6, only H of cyclobutane): **15a**: 3.92 (*ddd*, J = 0.8, 4.3, 8.2); 3.55 (*ddd*, J = 0.8, 10.0, 10.4); 3.07 (*ddd*, J = 1.4, 4.3, 10.0); 2.92 (*ddd*, J = 1.4, 8.2, 10.4); **15b**: 3.86 (*ddd*, J = 0.6, 7.2, 7.6); 3.59 (*t*, J = 7.6); 3.45 (*dd*, J = 0.6, 7.2, 7.6); 3.15 (*t*, J = 7.2); **15c**: 3.78 (*ddd*, J = 1.4, 6.4, 8.8); 3.63 (*ddd*, J = 1.4, 6.0, 8.4); 3.48 (*dd*, J = 6.0, 8.8); 3.32 (*dd*, J = 6.4, 8.4). The rel. configurations are unknown. MS: 272 (4, M^+), 74 (100).

Relative Conversion Measurements. In UV cells (*C*) $3 \cdot 10^{-4}$ M solns. of **1a**, **1b**, and **7** in MeCN were irradiated either in the absence of alkene or in the presence of a 100-fold mol-equiv. of either 2,3-dimethylbut-2-ene or dimethyl maleate. The rel. rates of disappearance of starting materials were monitored by UV, the absorbances being always > 1 during all measurements.

Sensitizer Experiments. Runs in the presence of indanone, xanthone, and benzophenone were run under conditions *A* and with thioxanthone under conditions *B*.

Stern-Volmer *Plots.* Naphthalene concentrations of up to 10^{-1} M were used under experimental conditions *A* and using a 'merry-go-round' setup. The rel. conversion of starting material to products was monitored by GC using tetradecane as internal standard.

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