1 h (as described for 13 → 15) to give 49 (1.22 g, 90%) as a syrup: TLC R_f 0.18 (A); $[\alpha]^{20}_D$ -19.15° (c 1.5, $CHCl_3$); ^1H NMR (60 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 3.0-4.3 (m, 9, H-1, H-1′, H-2, H-8, H-9′, H-9, H-4, H-5, H-6, H-6′), 5.5 (s, 1, H-7), 5.9 (bt, 1, J = 6.0 Hz, H-8), 7.4-7.5 (m, 5, C_6H_5). Anal. Calcd for $C_{21}H_{32}O_5Si$: C, 64.29; H, 8.16. Found: C, 64.12; H, 8.28.

1,5-Anhydro-4,6-*O*-benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-3-*C*-(((vinyloxy)methyl)methylene)-D-*ribo*-hexitol (50). Alcohol 49 (0.3 g) was converted into the title compound 50 in the standard way: TLC R_f 0.64 (A); $[\alpha]^{20}_D$ -18.6° (c 0.9, $CHCl_3$); ^1H NMR (80 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 5.5 (1, s, H-7), 5.75 (bt, 1, J = 6.2 Hz, H-8), 6.45 (dd, 1, $J_{10,11}$ = 7.0 Hz, $J_{10,11'}$ = 15.0 Hz, H-10). Anal. Calcd for $C_{23}H_{34}O_5Si$: C, 66.05; H, 8.14. Found: C, 66.21; H, 8.05.

1,5-Anhydro-4,6-*O*-benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-3-*C*-(formylmethyl)-3-*C*-vinyl-D-allitol (51). Compound 50 (0.15 g) was rearranged in 1.0 h according to the standard procedure to afford 51 (0.13 g, 85%) as a syrup: TLC R_f 0.58 (A); $[\alpha]^{20}_D$ -35.20° (c 0.7, $CHCl_3$); ^1H NMR (80 MHz) δ 0.08 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 2.4 (dd, 1, $J_{10,11}$ = 4.0 Hz, $J_{10,10'}$ = 17.0 Hz, H-10), 2.8 (dd, 1, $J_{10',11}$ = 2.0 Hz, H-10′), 3.35-3.8 (m, 6, H-1, H-1′, H-2, H-4, H-6, H-6′), 4.2 (m, 1, H-5), 5.30 (d, 1, H-9), 5.40 (s, 1, H-7), 5.45 (d, 1, H-9′), 6.25 ($J_{8,9}$ = 11.0 Hz, $J_{8,9'}$ = 17.5 Hz, H-8), 9.85 (dd, 1, H-11). Anal. Calcd for $C_{23}H_{34}O_5Si$: C, 66.04; H, 8.14. Found: C, 65.98; H, 8.20.

1,5-Anhydro-4,6-*O*-benzylidene-3-deoxy-3-*C*-(formylmethyl)-3-*C*-vinyl-D-allitol (52). Compound 51 (0.10 g) was desilylated in 1.5 h to give 52 (0.065 g, 90%) as a syrup: TLC R_f 0.32 (D); $[\alpha]^{20}_D$ -24.2° (c 1.2, $CHCl_3$); ^1H NMR (80 MHz) δ 2.2 (dd, 1, $J_{10,11}$ = 4.0 Hz, $J_{10,10'}$ = 17.5 Hz, H-10), 2.7 (dd, $J_{10',11}$ = 2.0 Hz, H-10′), 5.45 (s, 1, H-7), 6.25 (dd, 1, $J_{8,9}$ = 10.0 Hz, $J_{8,9'}$ = 16.0 Hz, H-8), 9.8 (dd, 1, H-11). Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.13; H, 6.38. Found: C, 67.29; H, 6.42.

Acknowledgment. We are grateful to the National Institutes of Health (GM 32569), Merck, Sharp and Dohme, and Ciba Geigy for support of this work.

Registry No. 1, 3162-96-7; 2, 89872-82-2; 3, 89872-83-3; 4, 89920-65-0; 5, 78329-22-3; 6, 89889-10-1; 7, 89872-84-4; 8, 89872-85-5; 9a, 89872-86-6; 9b, 78329-23-4; 10, 78329-24-5; 11 (isomer 1), 89920-66-1; 11 (isomer 2), 89920-67-2; 12, 78329-10-9; 13, 78342-22-0; 14, 89873-09-6; 15, 89920-68-3; 16, 78342-23-1; 17a, 78329-14-3; 17b, 78329-16-5; 18a, 34266-73-4; 18b, 19272-50-5; 19, 89872-87-7; 20, 89872-88-8; 21, 89872-89-9; 22, 78342-34-4; 23, 78342-35-5; 24, 6752-49-4; 25, 89920-69-4; 26, 90024-28-5; 27, 78329-18-7; 28, 78342-30-0; 29, 89872-90-2; 30, 89872-91-3; 31, 89872-92-4; 32, 89872-93-5; 33, 89872-94-6; 34, 89872-95-7; 35, 572-09-8; 36, 13137-69-4; 37, 154-58-5; 38, 65190-39-8; 39, 89872-97-9; 40, 89872-96-8; 41, 89872-98-0; 42, 89873-03-0; 43, 89872-99-1; 44, 89889-00-9; 45, 89873-01-8; 46, 89873-00-7; 47 (isomer 1), 89873-02-9; 47 (isomer 2), 89920-70-7; 48, 89873-04-1; 49, 89873-05-2; 50, 89873-06-3; 51, 89873-07-4; 52, 89873-08-5; Ph_3P=CHCOOEt, 1099-45-2; CH_2=CHOEt, 109-92-2.

Photochemical Reactivity of α-Sulfonyloxy Enones: An Easy Method for Arylation of 1,2-Diketones

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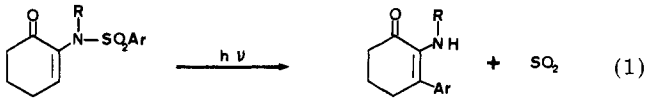
Received October 28, 1983

3-Aryl-1,2-cyclohexanediones 4 are prepared conveniently by photolysis of the corresponding 2-((arylsulfonyl)oxy)cyclohex-2-enones 1. The reaction was shown to occur from a triplet excited state. A biphotonic process involving the normal photo-Fries product 14 as an intermediate was ruled out by preparing and irradiating this compound. The difference of reactivity between 1 and 2-((arylsulfonyl)amido)cyclohexenones is discussed.

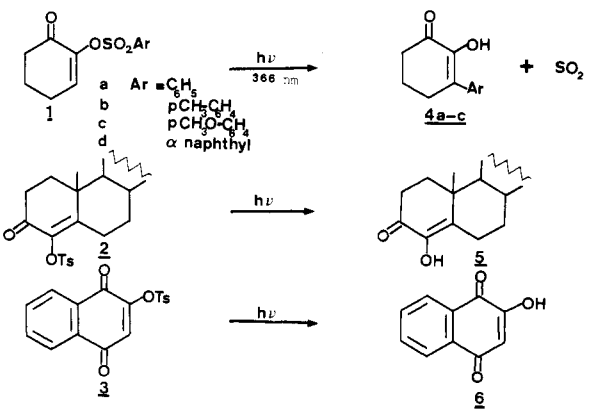
Photochemistry of conjugated enones depends strongly on the substitution.[1] With α-alkoxy or α-alkylamino groups the usually observed photocyclization products arise from the first singlet excited state of the enone. With α-*N*-(arylsulfonyl)amido substituents, a new photochemical reaction involving desulfonation and migration of the arene group to the β position was observed[2] (eq 1). In contrast



(1)

to the photocyclization this reaction was shown to occur from the lowest triplet state. If a similar process could be observed from α-(sulfonyloxy)cyclohexenones, 3-arylated 1,2-cyclohexanediones could be easily obtained from the unsubstituted diketone. Such α-aryl diones might be interesting intermediates in organic synthesis.[3] To check this idea, we prepared diketones 1-3 (Scheme I) and we report that desulfonation and migration of the aryl group

Scheme I



are indeed observed during the photolysis of 2-(arysulfonyl)oxy)-2-cyclohexenones and we discuss the scope

†Equipe de Recherche Associée au CNRS "Réarrangements thermiques et photochimiques" No. 688.

(1) Arnould, J. C.; Enger, A.; Feigenbaum, A.; Pete, J. P. *Tetrahedron* **1979**, *35*, 2501 and references cited therein.

(2) (a) Arnould, J. C.; Cossy, J.; Pete, J. P. *Tetrahedron* **1980**, *36*, 1585. (b) Cossy, J.; Pete, J. P. *Tetrahedron* **1981**, *37*, 2287.

0022-3263/84/1949-2355$01.50/0

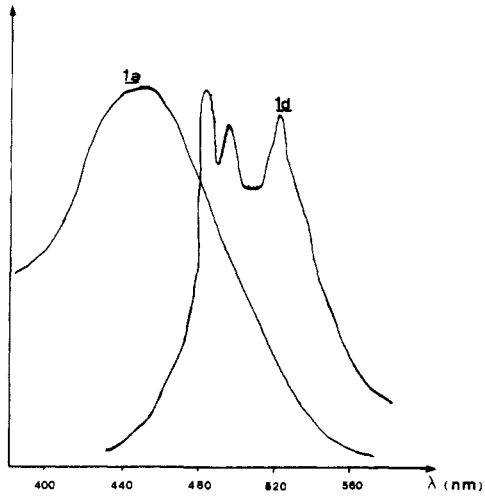


Figure 1. Emission spectrum of **1a** and **1d**.

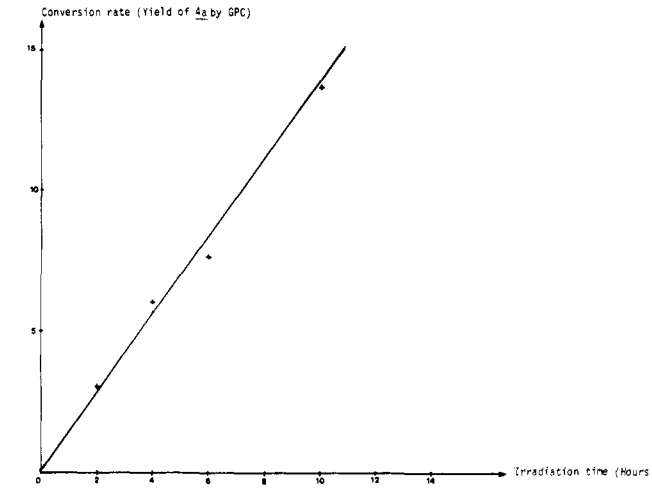
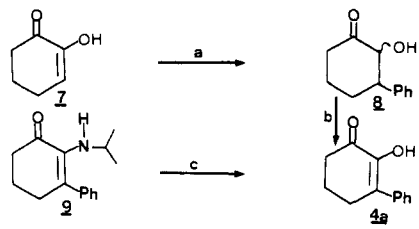


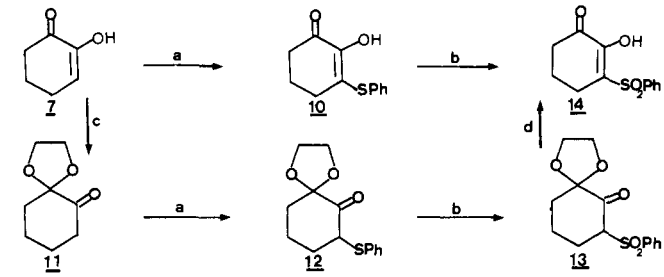
Figure 2. Direct irradiation of **1a** (10^{-2} M in MeCN).

Scheme II[a]



[a] a, PhMgBr[4] or PhMgBr, catalyst CuCl; b, Bi_2O_3[5] or $Cu(OAc)_2$[6]; c, CH_3COOH, H_2O.

Scheme III[a]



[a] a, (1) i-Pr_2NLi-THF, −78 °C, (2) PhSSPh; b, m-$ClC_6H_4CO_3H$, ether; c, CH_2OH-CH_2OH, PhH (H^+); d, CH_3COCH_3, H_2SO_4.

and the limits of this reaction.

Results

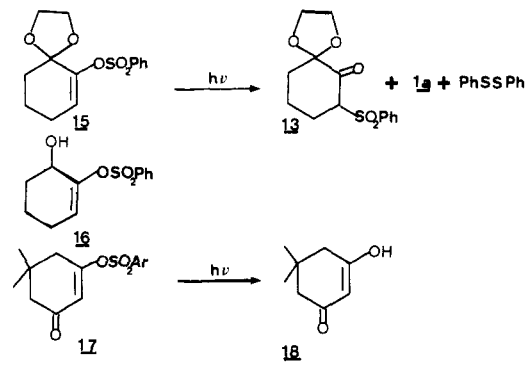
The starting ketones **1–3** were easily prepared by treating the unsubstituted diones with arenesulfonyl chloride in the presence of a base. The absorption spectra of these enones can be considered to be the superposition of the spectra of the corresponding enone and the arenesulfonyl chromophores. An emission spectrum of low intensity was detected when **1a** or **1d** were excited at 290 and 320 nm, respectively (Figure 1). The phosphorescence of the naphthyl group, observed by excitation of **1d** at a wavelength where all the light was absorbed by the enone chromophore, implies that an energy transfer to the naphthyl group was possible.

Irradiation of an ether–methanol (1:9) solution of 1a at 366 nm afforded SO_2 and 2-hydroxy-3-aryl-2-cyclohexenone **4a** in 63% isolated yield. Similarly, **4b** (45%) and **4c** (50%) were the main products obtained from **1b** and **1c**, respectively. No reaction was observed when **1d** was irradiated under similar conditions. Irradiation of the β-alkylated enone **2** and of naphthoquinone derivative **3** did not give the desulfonation arylation process; instead, the corresponding ketones **5** and **6** were formed by loss of the arenesulfonyl group.

The structures of the products **4–6** follow from their spectroscopic properties and comparison with authentic samples for **4a** (Scheme II), **5**, and **6**.

The reaction of desulfonation and migration of the aryl group observed during the photolysis of ketones **1** or **2**-(arylsulfonamido)-2-cyclohexenones contrasts with the expected photo-Fries rearrangement of enesulfonamides.[7]

Scheme IV



To determine if the photo-Fries product **14** was an intermediate in a biphotonic process, we prepared this compound according to Scheme III and we irradiated **14** in the preceding conditions. The desulfonated product **4a** could not be detected from the complex reaction mixture thus obtained. Furthermore, the product **4a** could have been detected by GPC even at very low conversion yields (Figure 2) which rules out a biphotonic process.

It has been shown previously that the desulfonation and aryl migration of 2-(arylsulfonamido)cyclohexenones results from the radical behavior of the triplet excited state of the cyclohexenone. In order to check which structural units are needed to observe such a desulfonation-arylation reaction we have considered the photochemical reactivity

(3) Part of this work appeared in a short communication: Feigenbaum, A.; Pete, J. P.; Scholler, D. *Tetrahedron Lett.* **1979**, 537.
(4) Tomboulian, P.; Bloomquist, C. A. A. *J. Org. Chem.* **1959**, *24*, 1239.
(5) Rigby, W. *J. Chem. Soc.* **1951**, 793.
(6) Blomquist, A. T.; Goldstein, A. "Organic Syntheses"; Wiley: New York, 1963; Collect Vol. IV, p 838.
(7) (a) Bellus, D. "Advances in Photochemistry"; Wiley, Interscience: New York, 1971; Vol. 8, p 109. (b) Graftieaux, A.; Gardent, J. *Tetrahedron Lett.* **1972**, 3321.

of **15**, **16**, and **17** (Scheme IV).

Compounds **15** and **16** which have no carbonyl groups might also lead to relaxed excited states with a distorted double bond.[8] When irradiated, the ketal **15** gave the α-keto sulfone **13** by a photo-Fries rearrangement, the deketalized starting material **1a**, and diphenyl disulfide, a dismutation product of the radical $C_6H_5SO_2^{\cdot}$.[9] Under the same conditions **16** gave a very complex reaction mixture. In no case, could the expected desulfonation-arylation product be detected. Irradiation of enone **17**, bearing the (arylsulfonyl)oxy group β to the carbonyl, gave the dimedone even in an anhydrous solvent.[10]

To determine the nature of the reactive excited state involved in the photochemical transformation of **1a** we carried out sensitization and quenching experiments. We determined that *p*-methoxyacetophenone (E_T = 298.9 kJ) sensitized the reaction of **1a**. Furthermore, a linear Stern–Volmer plot ($k_q\tau$ = 38 M^{-1}) was obtained when increasing amounts of naphthalene (E_T = 254.6 kJ) were introduced into the reaction mixture. If we consider the quenching by naphthalene to be diffusion controlled, we can deduce an approximate value of the triplet lifetime of **1a** ($\tau_T = 4.75 \times 10^{-9}$ s).

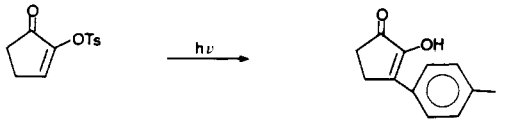
Furthermore and in contrast with the results obtained with 2-(arylsulfonamido)cyclohexenones, we have shown that there is no significant contribution of a radical chain process in this desulfonation-arylation reaction. The quantum yield measured for **1a** (Φ_{4a} = 0.05 at 254 nm) did not depend on the concentration and the reaction was not initiated by Bu_3SnH.[16]

Discussion

Direct α-arylation of ketones can be realized by various methods.[11] However, α-diketones are not easily arylated and the described methods are not very efficient. For example, reaction of phenylmagnesium bromide on 1,2-cyclohexanedione[4] gave only low yields of the ketol **8**. In the presence of catalytic amounts of cuprous chloride, we found an important enhancement of the reactivity; the transformation of the starting material was complete within a few minutes at 0 °C but the yield of **8** (30%) was only slightly improved (Scheme II).

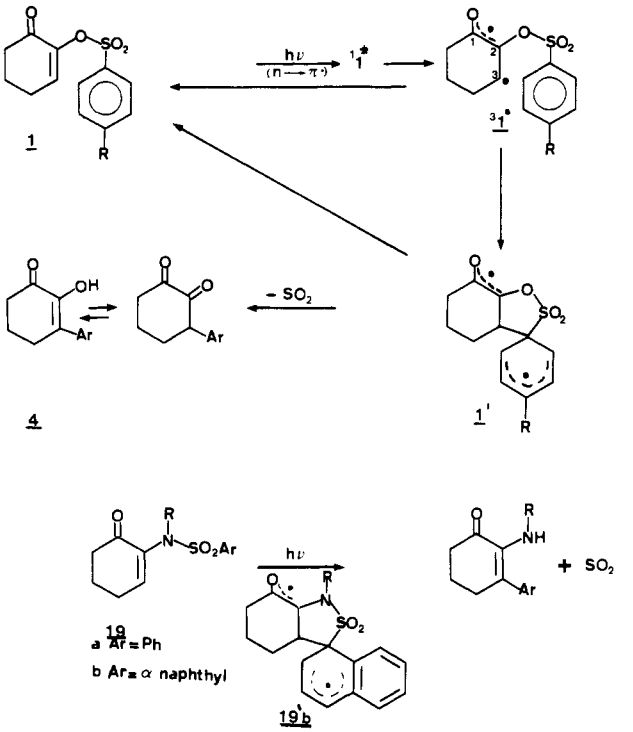
The photochemical method presented in this paper is very attractive: 2-((arylsulfonyl)oxy)cyclohexenones are quantitatively obtained from the corresponding 1,2-diones and the irradiation step, which can be realized easily on a 10-g scale, gives the expected aryl dione in an overall yield of about 50% based on cyclohexanedione.

Recently, this methodology was successfully applied to a synthesis of isolaurene from cyclopentanedione, and it was shown that the desulfonation arylation occurred in this case as for **1**[12] (eq 2).



(2)

Scheme V



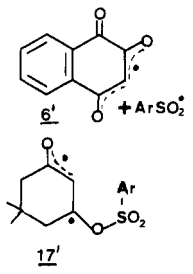
The sensitization and quenching experiments carried out to determine the nature of the reactive excited state indicate without ambiguity that the lowest triplet of **1a** is the only excited state involved in the desulfonation–arylation reaction. The kinetics of appearance of **4a** and the complex reaction mixture obtained during the photolysis of the photo-Fries product **14a** exclude a biphotonic process and the intermediacy of **14**. Finally, the absence of a concentration effect on the efficiency of the formation of **4a** and the failure to induce the desulfonation–arylation process by using radical chain initiators lead us to propose the mechanism shown on Scheme V as the most probable for the reaction.

The relaxation of the lowest-triplet excited state of cyclohexenone and cyclopentenone gives transients identified as orthogonal or twisted-triplet state, the angle of twisting varying with the rigidity of the molecule.[13] Such relaxed triplets should be available from other cyclohexenones such as **1** and should be considered as biradicals. The delocalization of one electron into the carbonyl group and the captodative effect[14] on C_α might increase the radical character of the C_3 carbon atom. Cyclization of this species to the aryl group should lead preferentially to a five-membered ring biradical **1'**[15] which can either revert to starting material or give **4** after extrusion of SO_2 and rearomatization. Such a behavior, which has been proposed for the analogous photodesulfonation of **19**, is very similar to what has been postulated by Speckamp[16] to rationalize the cyclization observed for 2-(iodomethyl)-*N*-(arylsulfonamido)piperidines.

This scheme is compatible with the lack of reactivity of **1d** and the absence of the desulfonation–arylation process

(8) For example, see: Bonneau, R.; Joussot-Dubien, J.; Salem, L.; Yarwood, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 4329.
(9) Pete, J. P.; Portella, C. *J. Chem. Res., Synop.* **1979**, 20; *J. Chem. Res. Miniprint* **1979**, 209.
(10) For an irradiation in the presence of water see: de Mayo, P.; Wasson, J. *J. Chem. Soc., Chem. Commun.* **1967**, 970.
(11) (a) Saito, R.; Izumi, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1776. (b) Heck, R. F. *Organomet. Chem. Synth.* **1972**, *1*, 455. (c) Kelly, L. F.; Narula, A. S.; Birch, A. J. *Tetrahedron* **1982**, *38*, 1813. (d) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1449. (e) Barton, D. H. R.; Charpiot, B.; Motherwell, W. B. *Tetrahedron Lett.* **1982**, *23*, 3365. (f) Kosugi, M.; Hagiwara, I.; Sumiya, T.; Migita, T. *J. Chem. Soc. Chem. Commun.* **1983**, 344.
(12) Tomari, K.; Machiya, K.; Ichimoto, I.; Ueda, H. *Agric. Biol. Chem.* **1980**, *44*, 2135.
(13) Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816.
(14) Viehe, J. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 917.
(15) (a) Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386. (b) Beckwith, A. L. J. *Spec. Publ. Chem. Soc.* **1970**, *24*, 239.
(16) (a) Speckamp, W. N.; Köhler, H. J. *J. Chem. Soc., Chem. Commun.* **1978**, 166. (b) Köhler, H. J.; Speckamp, W. N. *Tetrahedron Lett.* **1977**, 631; *J. Chem. Soc., Chem. Commun.* **1980**, 142.

Chart I



for **2**, **3**, **15**, and **17**. The naphthyl substituent of **1d** is responsible of the deactivation of the triplet excited state. At 77 K, we observe a phosphorescence spectrum characteristic of a naphthyl group even when the enone chromophore of **1d** was selectively excited at 365 nm. At room temperature the energy located on the naphthyl group could be dissipated by intersystem crossing and possibly through the biradical 1′. With 2-(naphthylsulfonamido)-cyclohexenone **19b** a similar emission spectrum was recorded despite a completely different reactivity and especially the formation of a desulfonation–arylation product.[2b] The energy of the lowest triplet excited state is very similar for **1d** and **19b**. The different photochemical behavior of these two molecules might reflect the difference of O–S and N–S bond energies. Indeed, this difference has been shown to induce different processes during the photolysis of arenesulfonates and arenesulfonamides. Whereas the S–N bond is exclusively cleaved by excitation of arenesulfonamides, the S–C bond between the arene and the SO_2 group is selectively cleaved by photolysis of arenesulfonates.[17] The higher energy of the S–O compared with the S–N bond explains also the failure of the attempted radical-induced desulfonation for **1a**. Although the radical induced desulfonation in the presence of tri-*n*-butyltin hydride (TBH) is observed for **19**,[2b] **4a** is not formed by irradiation of **1a** in the presence of TBH.

The photolysis of enones **2**, **3**, and **17** gave the desulfonylated ketones **5**, **6**, and **18**, respectively, rather than the expected α-aryl ketones.

Examination of molecular models show that it is impossible for the aromatic carbon bound to sulfur to approach the radical site of **2** in its distorted triplet state to allow the formation of a biradical like 1′. Steric repulsion is then too large. On the other hand, this approach is very easy for ((arylsulfonyl)oxy)cyclohexenones or cyclopentenones.

For **3**, the large stabilization of the radical pair formed by an S–O cleavage probably favors the observed fragmentation (Chart I).

From **17**, the twisted excited state should have the structure 17′. The delocalization of one electron into the carbonyl group lowers the reactivity of C_2 compared to that of ^{3}**1*** for an ipso substitution on the aryl group. Other processes, such as fragmentation, usually observed simultaneously with photo-Fries rearrangements become competitive and explain the formation of **18**. The absence of desulfonation–arylation processes from **15** and **16** and the photo-Fries rearrangement from **15** indicate the importance of the carbonyl group on the course of the reaction.

Experimental Section

^{1}H NMR spectra were recorded on a Varian A 60 instrument with Me_4Si as internal standard. IR spectra were obtained with a Pye Unicam SP 2000 spectrometer. For UV spectra, we used a Beckman ACTA III spectrophotometer. Mass spectra were obtained from UER Pharmacie, Reims. Melting points were determined on a Kofler Bank and are not corrected. Compounds were characterized by elemental analysis with an accuracy of ±0.3% when indicated. Irradiated solutions were bubbled with N_2 purified on Fluka's BTS-Katalysor.

Irradiation devices include the following: [1] Philips HPW 125 lamp (λ = 365 nm); [2] Hanau TQ 150 lamp, Pyrex filter (λ ≥ 300 nm); [3] Hanau TQ 150 lamp, wood glass filter (λ = 365 nm); [4] Hanau TQ 150 lamp, pyrex vessel + 10% methanolic acetone (λ > 310 nm); [5] Hanau TNN 15 lamp, quartz vessel (λ = 254 nm); [6] 12 Philips TUV 15 lamps, quartz vessel (λ = 254 nm); [7] Philips HOQ lamp, Pyrex vessel (λ ≥ 300 nm); [8] Philips HOQ lamp, potassium chromate (0.2 g/L) potassium carbonate (50 g/L) (λ = 313 nm).

Gas chromatographic analyses were performed on a GIRDEL 75 F D2 instrument with an FID detector. **4a** was determined on a 3% SE 30 column (1 m) at 180 °C (cholestane was used as internal standard). All yields indicated refer to isolated products.

Preparation of (Arylsulfonyl)oxy Enones 1, 2, 3, and 17. Typical Procedure for 1a–d, 3, and 17. To a solution of 1,2-cyclohexanedione (448 mg, 4 mmol) in acetone (80 mL) was added potassium carbonate (4 g, 28 mmol) and arenesulfonyl chloride (4 mmol). After stirring at room temperature for 24 h, the solution was filtered and the solvent evaporated under vacuum. A rapid chromatography (ether/pentane 1:1) separated the (arylsulfonyl)oxy enone (88% yield based on recovered starting material) and 1,2-cyclohexanedione (140 mg). Recrystallization from ether gave the product analytically pure with a usual yield of 60%.

Procedure for 2. 3,4-Cholestanedione (400 mg, 1 mmol), toluenesulfonyl chloride (200 mg, 1.05 mmol), and pyridine (5 mL) were left overnight at room temperature. **2** was separated from unreacted starting material by column chromatography and recrystallized from a 1:1 acetone/ethanol mixture: overall yield, 80%.

1a: mp 62 °C; $C_{12}H_{12}O_4S$ (C, H); NMR ($CDCl_3$) 7.5–8.2 (m, 5 H), 6.8 (1 H, t, J = 4.5 Hz), 2.5 ppm (6 H, m); IR ($CHCl_3$) 1700, 1650, 1450, 1385–1370, 1195, 1140, 1090, 910 cm^{-1}; UV (ether) λ_{max} 225 (ε 10000), 277 (ε 2000), 313 nm (ε 40); mass spectrum 252 (M^+, 14%), 188 (20%), 141 ($PhSO_2^+$, 100%), 77 (81%), 55 (34%).

1b: mp 62 °C; $C_{13}H_{14}O_4S$ (C, H); NMR (CCl_4) 7.57 (4 H, A_2B_2 spectrum, δ_A = 7.81, δ_B = 7.32 ppm, J_{AB} = 8.5 Hz), 6.8 (1 H, t, 4.5 Hz), 2.42 ppm (3 H, s); IR (CCl_4) 1703, 1637, 1598, 1370, 1360, 1192, 1180, 1140, 1088, 910 cm^{-1}; UV (ether) λ_{max} 225 (ε 23000), 274 (ε 3000) 313 nm (ε 118); mass spectrum 266 (M^+, 5%), 202 (10%), 155 ($MeC_6H_4SO_2^+$, 65%), 91 (100%).

1c: mp 96 °C; $C_{13}H_{14}O_5S$ (C, H); NMR ($CDCl_3$) 7.52 (4 H, A_2B_2 spectrum, δ_A = 7.82, δ_B = 7.22, J_{AB} = 9 Hz), 6.9 (1 H, t, J = 4.5 Hz), 3.9 ppm (3 H, s); IR ($CHCl_3$) 1700, 1600, 1500, 1375–1360, 1270, 1195, 1170, 1090, 910, 835, 810 cm^{-1}; UV (ether) λ_{max} 235 (ε 30000), 320 nm (ε 50); mass spectrum 282 (M^+, 12%), 172 (10%), 171 ($MeOC_6H_4SO_2^+$, 100%), 123 (12%), 107 (33%), 77 (11%), 55 (9%).

1d: mp 95 °C; $C_{16}H_{14}O_4S$ (C, H); NMR ($CDCl_3$) 9.7–5 ppm (7 H, m), 6.8 ppm (t, J = 4.5 Hz); IR ($CHCl_3$) 1710, 1640, 1385–1365, 1185, 1090, 910 cm^{-1}; UV (ether) λ_{max} 225 (ε 14000), 285 nm (ε 5700).

2: mp 123 °C; NMR (CCl_4) 7.59 (4 H, A_2B_2 spectrum, δ_A = 7.34, δ_B = 7.92 ppm, J_{AB} = 8 Hz), 2.47 (3 H, s), 1.25 ppm (3 H, s, 19-CH_3); IR (CCl_4) 1695, 1613, 1600, 1370, 1195, 1180 cm^{-1}; UV (ether) λ_{max} 231 (ε 20500), 274 (ε 500), 295 nm (ε 55).

3: mp 142 °C; NMR ($CDCl_3$) 8.2–7.2 (8 H, m), 6.9 (1 H, s), 2.45 ppm (3 H, s); IR ($CHCl_3$) 1670, 1650, 1600, 1395, 1300, 1260, 1200, 1180, 1100, 1070, 970 cm^{-1}; UV (ethanol) λ_{max} 226 (ε 22000), 330 nm (ε 3000).

17: oily; NMR (CCl_4) 7.63 (4 H, A_2B_2 spectrum, δ_A = 7.5 ppm, δ_B = 7.8 ppm, J_{AB} = 9 Hz), 5.83 (1 H, t, J = 1 Hz), 2.46 (3 H, s), 2.37 (2 H, d, J = 1 Hz), 2.18 (2 H, s), 1.0 ppm (6 H, s); IR (CCl_4) 1666, 1634, 1597, 1390, 1197, 1180, 1075, 960, 820 cm^{-1}; UV (ether) λ_{max} 227 (ε 23000), 274 (ε 620), 322 nm (ε 27).

Irradiations of (Arylsulfonyl)oxy Enones. Irradiation of (Arylsulfonyl)oxy Enones 1a–d. Typical Procedure. Enone **1** (16 mmol, approximately 4 g) in a 9:1 methanol–ether (500 mL) solvent mixture was irradiated (conditions 1) for 5 h. A specific and very sensitive revelation of aryl diones in the

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irradiation mixture on thin-layer chromatography is achieved by spraying with an alcoholic solution of iron trichloride. Crude reaction mixture was dissolved in methylene chloride and filtered on silica gel to remove polymeric material. The β-aryl diones were crystallized from ether–pentane solvent mixtures. Yields below are indicated for isolated products.

4a: 63% yield; mp 90 °C; $C_{12}H_{12}O_2$ (C,H); NMR ($CDCl_3$) 8.2–7.5 (5 H, m), 6.75 ppm (1 H, s); IR ($CHCl_3$) 3450, 1670, 1630, 1500, 1380, 1330, 1300, 1160 cm^{-1}; UV (ether) λ_{max} 225 (ε 6500), 305 nm (ε 17 000); mass spectrum 188 (M^+, 100%), 160 (25%), 117 (18%), 104 (16%), 91 (15%).

4b: 45% yield; mp 77 °C; NMR ($CDCl_3$) 7.38 (4 H, A_2B_2 spectrum, δ_A = 7.60 ppm, δ_B = 7.16 ppm, J_{AB} = 8.5 Hz), 2.35 ppm (3 H, s); IR ($CHCl_3$) 1665, 1375, 1160 cm^{-1}; mass spectrum 202 (M^+, 100%), 187 (60%), 174 (20%), 173 (10%), 159 (10%), 131 (15%), 118 (18%), 91 (15%).

4c: 50% yield; mp 129 °C; NMR ($CDCl_3$) 7.4 (4 H, A_2B_2 spectrum, δ_A = 7.8 ppm, δ_B = 7.0 ppm, J_{AB} = 9 Hz), 3.8 ppm (3 H, s); IR ($CHCl_3$) 3450, 1670, 1630, 1610, 1520, 1380, 1300, 1260, 1040, 835 cm^{-1}; UV (ether) λ_{max} 225 (ε 4000), 320 nm (ε 20 000); mass spectrum 218 (M^+, 100%), 190 (32%), 147 (15%), 134 (28%), 91 (14%), 77 (10%).

Irradiation of **1d** (conditions 1 or 6) resulted only in slow polymerization of starting material. No dione could be isolated or even detected by spraying with $FeCl_3$ on thin-layer chromatography.

Detection of SO_2. While irradiating **1b**, SO_2 was removed from the reactor by a nitrogen stream and led to a solution of $BaCl_2$ (1 g) and hydrogen peroxide (5 mL). A barium sulfate precipitate was thus observed.

Irradiation of 4-((Tolylsulfonyl)oxy)cholest-4-en-3-one (2). **2** (30 mg, 0.054 mmol) in ether (30 mL) was irradiated (conditions 8) for 20 h. Diosphenol **5** (13 mg, 60% yield) was isolated by preparative thin-layer chromatography and identified by comparison with an authentic sample.[18]

Irradiation of 2-((Tolylsulfonyl)oxy)-1,4-naphthoquinone (3). Irradiation of **3** (3×10^{-3} M) in methanol or ethanol (conditions 1) for 4 h gave only complex mixtures. When **3** (230 mg, 0.7 mmol) was irradiated in benzene (150 mL) (conditions 1) for 40 h, 2-hydroxy-1,4-naphthoquinone (**6**) was formed and isolated by preparative thin-layer chromatography (95 mg, 80% yield). **6** was identified by comparison with a commercially available sample.

Irradiation of 3-((Tolylsulfonyl)oxy)-5,5-dimethylcyclohex-2-enone (17). **17** (294 mg, 1 mmol) in anhydrous benzene (25 mL) was irradiated (conditions 6) for 2.5 h. From the complex reaction mixture we could isolate by preparative thin-layer chromatography, dimedone **18** (51 mg, 36%) identical with a commercial sample.

Preparation of 3-Phenylcyclohexane-1,2-dione 4a via Ketol 8. Addition of PhMgBr to Cyclohexanedione. To a suspension of copper chloride (2 mmol) in ether (2 mL) was added a solution of PhMgBr (20 mmol) in ether (20 mL). This is carried out under argon atmosphere, at room temperature, in a Schlenck tube. The solution was then cooled (0 °C) and cyclohexanedione (4 mmol) in tetrahydrofuran (10 mL) was dropped in while stirring. 40 min after the end of the addition, the reaction mixture was hydrolyzed with an aqueous solution of ammonium chloride. The organic phase is then washed with ammonia to remove copper and filtered. Ketol **8**[4] (1.27 mmol, 32%) was isolated by thin-layer chromatography. When the addition was made at room temperature, a very vigorous reaction took place, and the yield was only 15%.

The ketol **8** (480 mg, 2.5 mmol) was added to a solution of copper acetate (1 g, 5 mmol) in 50% acetic acid (3 mL) and methanol (0.25 mL). The mixture is heated until its temperature reaches 90 °C and allowed to cool very slowly. The solution was filtered on Hyflo and extracted with CH_2Cl_2 and the dione **4a** (100 mg, 35%) was separated from unreacted **8** (200 mg) by column chromatography.

Oxidation following the procedure indicated in ref 5 gave the dione **4a** with 10% yield.

Preparation of 4a via 2-(*N*-Isopropylamino)-3-phenylcyclohex-2-enone (9). Compound **9** (46 mg, 0.2 mmol) was heated over 30 min to 50 °C in acetic acid (5 mL). After extraction and preparative thin-layer chromatography, dione **4a** (12 mg, 40%) was isolated along with unreacted **9** (9 mg).

Dione **4a** prepared by this method was identical with a sample obtained from **1a** (melting point and spectroscopic data).

Synthesis of 3-(Phenylsulfonyl)cyclohexane-1,2-dione (14) from 1,2-Cyclohexanedione Monoketal (11). α-Sulfenyl-α'-(ethylenedioxy)cyclohexanone (12). Ketal **11**[19] (103 mg, 0.65 mmol) in a mixture of THF (1 mL) and HMPA (0.3 mL) was added at −50 °C to a solution of lithium diisopropylamide (0.72 mmol)[20] in THF (1 mL) in an argon atmosphere. The mixture was stirred for 1 h at room temperature. Diphenyl disulfide (159 mg, 0.72 mmol) was then added at −50 °C. After stirring for 1 h at room temperature, the reaction mixture was hydrolyzed with water and extracted with ether. The crude reaction mixture was chromatographed on a silica column. Diphenyl disulfide was eluted first with cyclohexane, and the α-sulfenyl ketone **12** was eluted with methylene chloride.

12: 45% yield; mp 77–78 °C (recrystallized from cyclohexane); NMR (CCl_4) 7.40 (5 H, m), 3.9 ppm (4 H, m); IR (CCl_4) 1740, 1590, 1200, 1150, 1125, 950, 900 cm^{-1}; mass spectrum M^+ 264 (8%), 236 (78%), 220 (8%), 135 (38%), 126 (37%), 110 (13%), 106 (10%), 99 (100%), 55 (30%).

Oxidation of 12 to 13. α-Sulfenyl ketone **12** (60 mg, 0.23 mmol) in methylene chloride (6 mL) was allowed to react with *m*-chloroperbenzoic acid (95 mg, 0.55 mmol) for 2 h at room temperature. 5% sodium hydrogen carbonate solution (10 mL) was then added and stirring was carried on for 1 h. The organic layer was then separated, the aqueous phase was washed with CH_2Cl_2. After the combined organic layers were dried, the solvent was evaporated and the keto sulfone **13** (57 mg) was recrystallized from ethanol.

13: 85% yield; mp 160 °C; NMR ($CDCl_3$) 8.5–7.5 (5 H, m), 4.0 ppm (5 H, m); IR (CCl_4) 1745, 1625, 1585, 1445, 1325, 1310, 1250, 1240, 1025 cm^{-1}; mass spectrum M^+· 296 (3%), 268 (10%), 155 (20%) (loss of $C_6H_5SO_2$), 154 (10%), 126 (22%), 100 (43%), 99 (100%).

Deketalization of 13. **13** (121 mg, 0.41 mmol) in acetone (20 mL) was refluxed with 6 N sulfuric acid (4 mL) for 4 h. Preparative thin-layer chromatography (eluent CH_2Cl_2–MeOH 98:2) allowed separation of diketo sulfone **14** (20 mg, 20%). **14** was identical with a sample prepared by other routes. **13** proved to be difficult to deketalize by other methods.[21]

Synthesis of 14 from Cyclohexanedione. 3-(Phenylthio)cyclohexane-1,2-dione (10). Cyclohexane-1,2-dione **7** (224 mg, 2 mmol) in THF (10 mL) was added at −78 °C to a solution of lithium diisopropylamide (prepared from 4.4 mmol of diisopropylamine and 4.4 mmol of BuLi) in THF (5 mL). After stirring 15 min at −78 °C, phenyl benzenethiosulfonate (500 mg, 2 mmol) in THF (5 mL) was added. Stirring was carried on 4 h and the reaction was hydrolyzed with 1 M HCl. **10** (50 mg) was then isolated by preparative thin-layer chromatography (eluent benzene–methylene chloride 2:1).

10: 11% yield; mp 130 °C; NMR ($CDCl_3$) 7.5 ppm (5 H, m), 6.6 ppm (1 H, broad); IR ($CHCl_3$) 3460, 1660, 1615, 1370, 1350, 1275, 1160, 1140 cm^{-1}; mass spectrum M^+· 220 (10%), 219 (20%), 218 (100%), 149 (30%), 141 (38%), 123 (15%), 112 (35%), 111 (20%), 110 (75%), 85 (35%), 78 (25%), 77 (25%).

3-(Phenylsulfonyl)cyclohexane-1,2-dione (14). **13** (26 mg, 0.12 mmol) in CH_2Cl_2 (4 mL) was treated at 0 °C with *m*-chloroperbenzoic acid (42 mg, 0.26 mmol) for 1.5 h. Benzoic acid was then removed by washing with sodium hydrogen carbonate solutions. After extraction and preparative thin-layer chromatography, **14** (10 mg, 30% yield) was isolated.

14: amorphous; NMR ($CDCl_3$) 8.4 (1 H, broad signal) 8.03 (2 H, m), 7.6 (3 H, m), 2.68 (2 H, t, J = 5 Hz), 2.58 (2 H, t, J = 5.5 Hz), 2.1 ppm (2 H, m); IR ($CHCl_3$) 3500–2800 (broad band), 1700 (broad, very strong), 1605, 1575, 1300, 1150, 815 cm^{-1}; UV (ether) λ_{max} 222 (ε 12 400), 278 (ε 7100); mass spectrum M^+· 252 (26%), 207 (12%), 156 (10%), 143 (20%), 139 (10%), 126 (64%), 125 (38%), 112 (16%), 111 (100%), 110 (26%), 93 (24%), 83 (52%),

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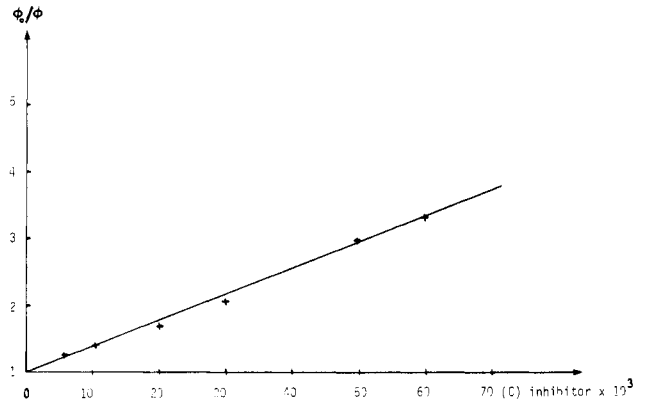

Figure 3. Stern–Volmer plot with naphthalene for inhibitor (λ 365 nm, **1a** 10^{-2} M in MeOH).

82 (29%), 78 (82%), 77 (64%), 55 (52%), 51 (35%).

Irradiation of 14. **14** (3×10^{-3} M) in methanol–ether (9:1) was irradiated for 0.5 h (conditions 1), together with a reference tube containing **1a** at the same concentration. Thin-layer and gas chromatography showed that **4a** was formed only in the reference tube. No trace of **4a** could be detected in the complex product mixture from irradiation of **14**.

2-((Phenylsulfonyl)oxy)cyclohex-2-enone Ethylene Ketal (15). Preparation of 15. **1a** was ketalized by following the typical experimental procedure[19] giving **15** (85% yield).

15: oily; NMR ($CDCl_3$) 8–7.2 (5 H, m), 5.83 (1 H, t, J = 4 Hz), 3.6 ppm (4 H, s); IR (CCl_4) 1670, 1450, 1380, 1360, 1190, 1180, 1120, 1080, 1075, 1025, 945, 900 cm^{-1}; UV (ether) λ_{max} 218 (ε 10700), 265 nm (ε 1000).

Irradiation of 15. **15** (300 mg, 1 mmol) was irradiated (conditions 6) in ether (170 mL) for 0.5 h. After evaporation of the solvent, thin-layer chromatography (cyclohexane–ethyl acetate 70:30) of the crude reaction mixture allows separation of diphenyl disulfide (16 mg, 15% yield), **1a** (45 mg, 18% yield), and the photo-Fries product **13** (45 mg, 16% yield). **13** was identical with a sample obtained by oxidation of **12**.

Reduction of 1a. 2-((Phenylsulfonyl)oxy)-2-cyclohexenol (16). **1a** (236 mg, 1 mmol)[22] was added to a solution of $CeCl_3 \cdot 6H_2O$ (354 mg, 1 mmol) in methanol (3 mL). $NaBH_4$ (38 mg, 1 mmol) was then added slowly, stirring was carried on for 5 min, and the reaction mixture was then extracted with water and ether. Alcohol **16** (238 mg) was thus obtained quantitatively.

16: mp 123 °C; ^1H NMR ($CDCl_3$) 8.2–7.4 (5 H, m), 5.5 (1 H, t, J = 4 Hz), 4.2 (1 H, broad), 2.8 ppm (1 H, broad); IR (CCl_4) 3530, 1675, 1450, 1375, 1265, 1190, 1180, 1092, 1070, 875, 835, 820 cm^{-1}.

Attempted Radical Initiation with Bu_3SnH. Enone **1a** (50 mg, 0.265 mmol) and Bu_3SnH (120 mg, 0.5 mmol) in benzene (20 mL) were irradiated at 365 nm (conditions 1) for 1 h. No aryl dione could be detected by thin-layer or by gas chromatography. In a reference tube containing **1a** without Bu_3SnH, significant amounts of **4a** were formed. In an other reference tube 2-(*N*-isopropyl-*N*-phenylsulfonamido)-2-cyclohexenone (**19**) at the same concentration was irradiated with an equal amount of Bu_3SnH.

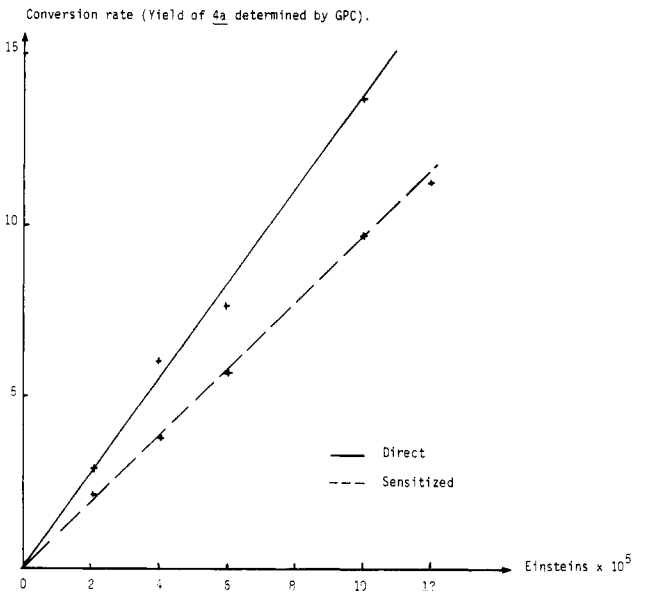

Figure 4. Direct and sensitized irradiation of **1a** (10^{-2} M in MeCN).

The desulfonation–arylation product was detected here after 7 min.

Kinetic Studies, Quantum Yields. Inhibition of 1a by Naphthalene. Seven Pyrex tubes, each containing 3 mL of **1a** (10^{-2} molar) in methanol and various concentrations in naphthalene, were irradiated for 8 h at 365 nm (conditions 3) on a merry-go-round apparatus. Dione **4a** was determined by GPC. The Stern–Volmer plot obtained is illustrated in Figure 3.

Sensitization of Formation of 1a by *p*-Methoxyacetophenone. Two quartz tubes containing enone **1a** (10^{-2} M) (ϵ_{254} 1400) in acetonitrile (3 mL) were irradiated together (conditions 5) one without, the other with *p*-methoxyacetophenone (1.5×10^{-2} M) (ϵ_{254} 15000). Under these conditions, 95% of the incident light was absorbed by the sensitizer. Chromatographic analysis and use of cyclopentanone as a chemical actinometer[23] showed that **4a** was formed by sensitization with a quantum yield of Φ_{sens} 0.035 (Figure 4).

Quantum Yield of Formation of 4a. **1a** was irradiated as in the preceding section. A plot of **4a** (determined by GPC) formed as a function of absorbed einsteins (Figure 4) gave quantum yield Φ_{254} 0.05.

Registry No. **1a**, 70871-42-0; **1b**, 70871-43-1; **1c**, 70871-44-2; **1d**, 90047-32-8; **2**, 70910-80-4; **3**, 70871-48-6; **4a**, 70871-45-3; **4b**, 70871-46-4; **4c**, 70871-47-5; **5**, 2066-10-6; **5** (dione), 90129-14-9; **6**, 83-72-7; **7**, 10316-66-2; **8**, 7015-14-7; **9**, 62297-26-1; **10**, 90047-36-2; **11**, 4746-96-7; **12**, 90047-34-0; **13**, 90047-35-1; **14**, 90047-33-9; **15**, 90047-37-3; **16**, 90047-38-4; **17**, 77708-65-7; **18**, 3471-13-4; **19**, 62297-17-0; PhBr, 108-86-1; $Cu(OAc)_2$, 142-71-2; Bi_2O_3, 1304-76-3; PhSSPh, 882-33-7; $PhSSO_2Ph$, 1212-08-4; $CeCl_3$, 7790-86-5; Bu_3SnH, 688-73-3; naphthalene, 91-20-3; *p*-methoxyacetophenone, 100-06-1.

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