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Photochemistry of 2-arenesulfonyloxy-2-cyclohexenone
A convenient α-arylation of 1,2-cyclohexanediones

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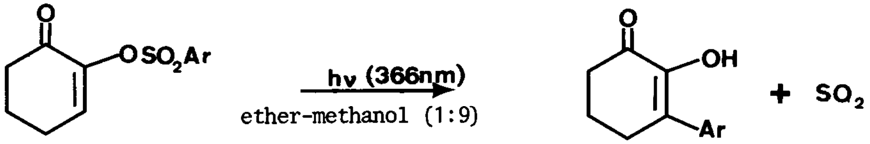
Previously we have shown that photolysis of 2-(N-alkylsulfonylamido)-cyclohexenones provides a facile method for the α-arylation of 1,2-cyclohexanediones (1). We now wish to report that 2-arenesulfonyloxy-2-cyclohexenones (2) show analogous photochemical behavior.

Irradiation of an ether methanol solution of 2-benzenesulfonyloxy-2-cyclohexenone 1a at 366 nm affords 2-hydroxy-3-phenyl-2-cyclohexenone 2a in 40% isolated yield. The structure of 2a was established by an independent synthesis (3). Irradiation of cyclohexenones

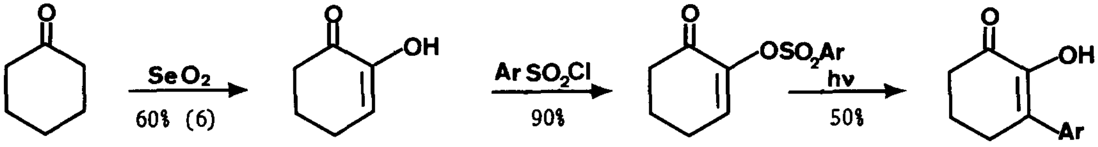


1 2

		Ar	
1	a :	C_6H_5	(40%)
	b :	p $CH_3C_6H_4$	(50%)
	c :	p $CH_3OC_6H_4$	(50%)
	d :	α-naphthyl	(–)

1b and 1c lead to parallel results. The structures of photoproducts 2b and 2c follow from their spectroscopic and analytical properties (4). It is to be noted that migration of the phenyl substituent occurs with retention of the original position of substitution on the aromatic ring. No reaction was observed when 1d was irradiated under identical conditions.

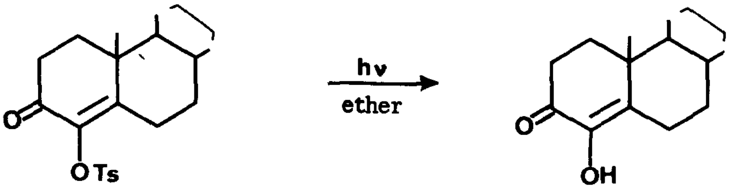
Although the chemical yield of 1 → 2 is only moderate, various phenyl-substituted 2-arylsulfonyloxy-2-cyclohexenones can be readily prepared from cyclohexanone by a 3-step sequence summarized below. Consequently 1 → 2 provides an easy and useful alternative synthetic entry to this class of compounds (3, 5).



1 2

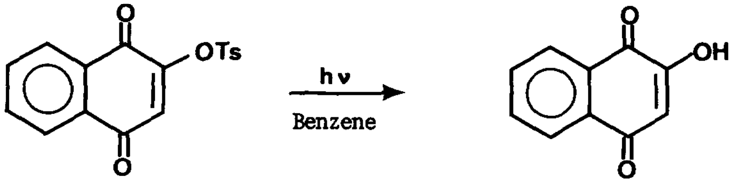
The quantum yield observed in the direct irradiation of 1a is wavelength dependent (Φ_{313} = 0,125 ; Φ_{254} = 0,05) and the reaction proceeds also in ether or benzene. When 1a is irradiated in the presence of p-methoxyacetophenone (E_T = 74 kcal) under conditions where the triplet sensitizer (7) is absorbing most of the incident light, the quantum yield for the sensitized formation of 2a is 0.035. Moreover, when 1a is irradiated in the presence of naphthalene (up to concentrations of 0.1 M of the quencher), a linear Stern-Volmer plot ($k_Q \tau = 38 \pm 5\ M^{-1}$) is obtained. These results suggest that only one excited state is involved in 1 → 2 and that it is a triplet state.

We have also found that the propensity for migration of the aryl group in 1 → 2 is sensitive to substitution at the position β to the carbonyl group. Thus, when 4-tosyloxy-cholest-4-en-3-one 3 is irradiated under the same conditions employed for 1 → 2, the desulfonylated compound 4 is the major product and no migration of the tolyl group to C-5 is observed. Moreover 2-hydroxynaphthoquinone is the major product obtained from irradiation of sulfonylated quinone 5.



3

4 (50%)



5

6 (80%)

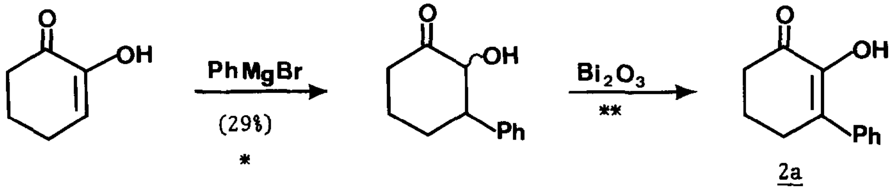
It might be suggested that irradiation of 1 proceeds by a photo-Fries rearrangement (8) to give a diketosulfone which photodecomposes into 2. However, sulfones are not detected in the reaction mixture and 2-arenesulfonylamido-2-cyclohexenones have a similar behavior (1). These results are not consistent with such an intermediate (10). Although the formation of 4 and 6 might suggest that S-O bond cleavage is the primary photochemical step, a mechanism involving a cyclization to a biradical intermediate is also possible (9). Work is continuing in our laboratory to determine the scope of this reaction and to verify the mechanism.

References:

1) J.C. Arnould, J. Cossy and J.P. Pete, Tetrahedron Letters, 3919 (1976).

2) The enones 1, 3 and 5 have been prepared by reaction of an arenesulfonylchloride with the appropriate diketone precursor.

3) 2a has been prepared according to the following scheme:



*P. Tomboulian and C.A.A. Bloomquist, J. Org. Chem. 24, 1239 (1959)
**according to W. Rigby, J. Chem. Soc. 793 (1951).

4) Satisfactory IR, NMR and mass spectra were obtained for the new compounds.

5) Alternative arylations of enolates have been recently reported

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J.F. Bunnett and J.E. Sundberg, J. Org. Chem. 41, 1702 (1976)

R.G. Scamehorn and J.F. Bunnett, J. Org. Chem. 42, 1457 (1977).

6) C.C. Hach, C.V. Banks and H. Diehl, Org. Synth., coll. Vol. IV, p. 229.

7) p methoxyacetophenone is not able to abstract efficiently hydrogen from the solvent. Thus it is apparent that the reaction does not proceed by chemical sensitization. P.J. Wagner Pure and Applied Chem. 49, 259 (1977).

8) D. Belluš Advances Photochem. 8, 109 (1971).

9) R. Loven and W.N. Speckamp Tetrahedron Letters, 1567 (1972).
J.J. Köhler and W.N. Speckamp Tetrahedron Letters, 631 (1977).

10) The linear plot giving the yield of 2a as a function of the irradiation time indicates that 2a is probably a primary photoproduct for direct and the sensitized irradiations of 1a.

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