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PHOTOLYSIS OF 2(N-ALKYL-ARYLSULFONYLAMIDO) CYCLOHEXENONE
AN UNUSUAL AND USEFUL DESULFONATION REACTION (1)

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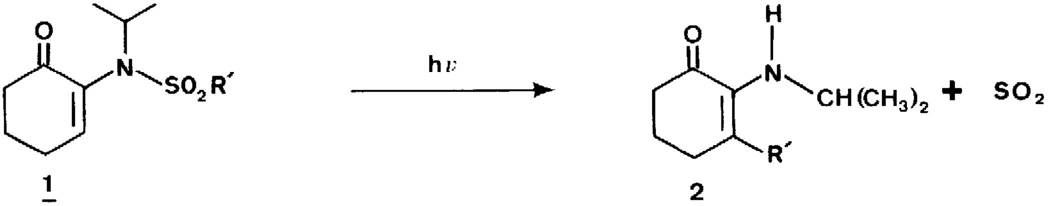
In previous work, we have shown that alkylidene azetidinols and α-ketoazetidines are produced in good yield from 2(N-alkyl-arylsulfonylamido)cyclohexenones (2). However, this reaction is very sensitive to the operating conditions and to the substitution pattern of the substrate ; for example, when the nitrogen in 1 bears an isopropyl group, a desulfonation reaction (equation |1|) is the only observed process, along with polymer formation.

Reaction |1|



In the present study, we describe this unusual reaction and its generality ; our results support radical intermediates during the photolysis.

As shown in table 1, reaction |1| is very general for a wide variety of N-arenesulfonyl and even N-alkylsubstituents. Structure 2 is attributed on the basis of its characteristic spectral properties : IR and UV spectra indicate the presence of conjugated enone and IR band at 3320 cm^{-1} is evidence of a secondary amine which is confirmed by the proton NMR spectrum. NMR also reveals the absence of vinylic protons. ^{13}C NMR and mass spectra are in accord with the assignment. The evolution of sulfur dioxide during the reaction has been demonstrated in the usual manner (3).

Table 1

R	SO_2-R'	yield % in ether 313 nm	yield % in benzene 254 nm
Ethyl	T_S	25	40
Benzyl	T_S	10	40
Allyl	T_S	15	30
Isopropyl	T_S	40	70
Isopropyl	SO_2-C_6H_5	30	65
Isopropyl	α-SO_2-naphthyl	40	50
Isopropyl	β-SO_2-naphthyl	35	60
Ethyl	α-SO_2-naphthyl	50	40
Ethyl	β-SO_2-naphthyl	40	50
Isopropyl	SO_2-CH_3	0	0

$|1| = 10^{-2}$ à $2 10^{-2}$ M

The yield of the arylated compound 2 which depends on the irradiation conditions is sufficiently high to be of interest synthetically. The migration of the aryl occurs indeed with retention of the position of substitution on the aryl group.It would have been interesting to generalize reaction |1| to alkylsulfonylderivatives of 1 ; unfortunately,replacement of the arenesulfonyl by methanesulfonyl considerably reduces reactivity and completely suppresses the desulfonation.

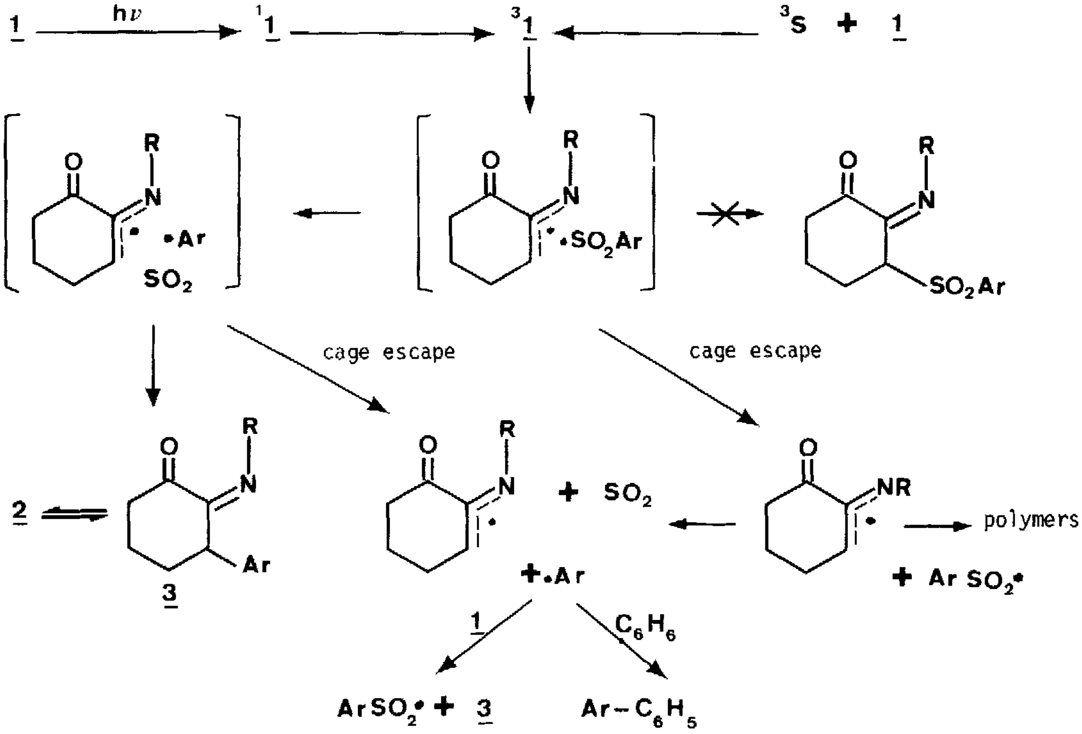
Excited state involved in the reaction :

Table 1 shows that reaction |1| is sensitized by benzene and benzophenone(10); further Michler's ketone is also an efficient sensitizer of the desulfonation of 1 when R' is naphthyl These sensitisation experiments mean that a triplet state of 1 may induce reaction |1| , to determine if a triplet is the only excited state responsible for this new reaction we have performed quenching experiments. When 1 (R' = α-naphthyl) is photolyzed in the presence of iron^{III} acetylacetonate (E_T = 30 kcal/mol) as quencher (4) the linear Stern Volmer plot obtained ($k_Q\tau$ = 200 M^{-1}) indicates that only one state is likely to be involved and that it is a triplet state (5).

Mechanism of the reaction :

Arenesulfonyl radicals are known to be produced in the photolysis of arenesulfonates and arenesulfonylamides (6) and are probable intermediates in the photolysis rearrangement of arenesulfonylderivatives of aniline (7). It seems probable that breaking of the N-S bond with formation of a pair of radicals occur from 1 in a triplet excited state and we thus propose the mechanism shown in table 2 for this reaction.

Table 2



Evidence for a radical pair and for the diffusion of radicals from a solvent cage is obtained from the following observations :

When 1 (R' = α-naphthyl) is photolyzed at 254 nm, compound 2 is formed with a quantum yield (ϕ=2) higher than unity , which is indicative of participation of a chain process (8). Further, if bimolecular processes are involved in the formation of 2, the quantum yield of 2 ought to be sensitive to the concentration of starting material , we have shown that this is indeed the case for 1 (R' = pCH_3-C_6H_4). Finally, biphenyl derivatives are characterized in the reaction when benzene is used as sensitizer and solvent, however the high yields of 2 under these conditions , although phenyl radicals react rapidly with benzene (9), show that the reaction proceeds mainly in a solvent cage.

Owing to the easy access to starting material, the present study has thus demonstrated that photolysis of 2(N-alkyl-sulfonylamido) cyclohexenones constitutes a simple and interesting method for the arylation of cyclohexanediones derivatives.

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5) These results are confirmed by the observation that triplet quenchers are able to quench reaction |1| but not the cyclisation to ketooxetanes and alkylidene oxetanols also observed from 2-tosylethylamido cyclohexenones.

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8) When R' ≠ α-naphthyl (ϕ=2) is always lower than unity

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10) If benzophenone has been shown, by VPC, to be an efficient sensitizer of the reaction in every case, the yield for apparition of 2 has not been determined with accuracy and the quantum yield of sentisation has only be measured for R = iPr and R' = p $CH_3-C_6H_4$ (Φ_{sens} = 0.2).