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PHOTODECOMPOSITION OF SELENOSULFONATES AND THEIR FACILE PHOTOADDITION TO ALKENES[1]

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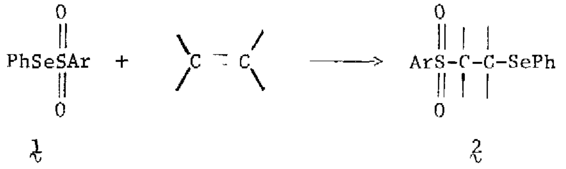
Abstract Phenyl areneselenosulfonates (**1**) are very photosensitive and easily undergo photodecomposition via initial homolysis of the Se-S bond. In the presence alkenes this facile photodissociation of **1** can be used to initiate a free radical chain reaction (eq 6) that leads to addition of **1** to the alkene to form β-phenylselenosulfones (**2**). The photoaddition requires much shorter reaction times than the non-photolytic addition of **1** to alkenes described recently.[2]

Both Back and Collins[2a] and Kobayashi and Miura[2b] have recently reported that Se-phenyl areneselenosulfonates (**1**) will add to olefins (eq 1) to give β-phenylselenosulfones (**2**). Reactions were effected either at room temperature in methylene chloride with boron trifluoride etherate as catalyst[2a] or at reflux in benzene[2ab] or chloroform[2a] without catalyst. Rather long reaction times (18-72 hrs) were required.

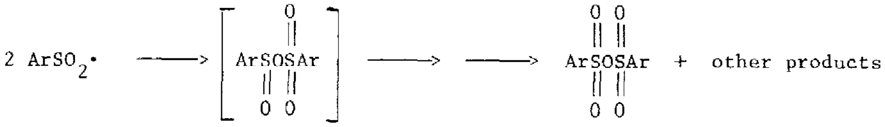


(1)

We have found that **1** are unusually photosensitive. Thus, although a deaerated solution of **1** (0.3 M) in carbon tetrachloride shows no detectable decomposition after 24 hrs in the dark at room temperature, after 24 hrs under laboratory fluorescent light significant decomposition of **1** is evident, and if irradiated for 7 hrs in pyrex in a Rayonet reactor (RPR-2537 lamp) photodecomposition of **1** is complete. The identifiable products of the photodecomposition of **1** (1 mmol, Ar = p-$CH_3C_6H_4$) under these conditions are diphenyl diselenide (0.41 mmol) and the arenesulfonic anhydride, $ArSO_2OSO_2Ar$ (0.32 mmol). These products are believed to arise as the result of a reaction sequence (eqs 2-5) initiated by the photodissociation of **1** into a PhSe· and an $ArSO_2$· radical (eq 2).[3]

$$PhSeSO_2Ar \xrightarrow{h\nu} PhSe\cdot + ArSO_2\cdot \qquad (2)$$

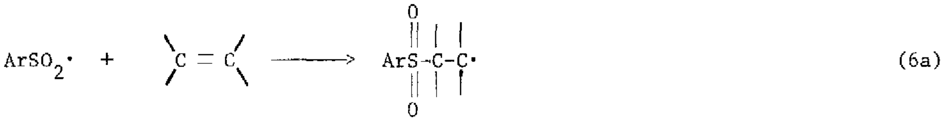
$$PhSe\cdot + PhSeSO_2Ar \longrightarrow PhSeSePh + ArSO_2\cdot \qquad (3)$$



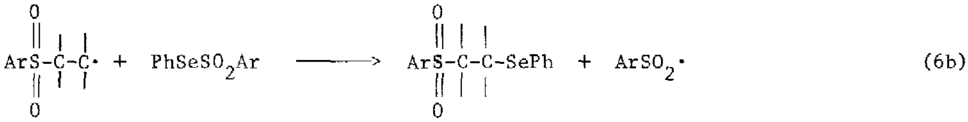
$$2\,ArSO_2\cdot \longrightarrow \left[Ar\underset{O}{\underset{\|}{S}}O\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}Ar \right] \longrightarrow \longrightarrow Ar\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}O\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}Ar + \text{other products} \qquad (4)$$

$$2\,PhSe\cdot \longrightarrow PhSeSePh \qquad (5)$$

We have also found that in the presence of suitable alkenes this facile photodissociation of **1** can be used to initiate a free radical chain reaction (eq 6) that results in the addition of **1** to the alkene to yield **2** (eq 1). Products (and product yields) for photoaddition of **1** to several simple alkenes are shown in Table I. That the photoaddition is a chain reaction is shown by the fact that the reaction time required (<1.5 hrs) is considerably shorter than the 7 hrs needed for the photodecomposition of **1** in the absence of the alkene. That free



$$ArSO_2\cdot + \;>C=C<\; \longrightarrow Ar\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \qquad (6a)$$



$$Ar\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + PhSeSO_2Ar \longrightarrow Ar\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-SePh + ArSO_2\cdot \qquad (6b)$$

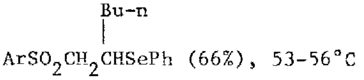
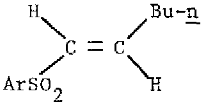
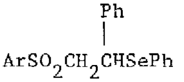
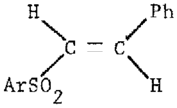
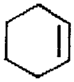
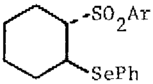
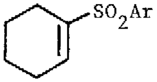
radical intermediates are involved is further indicated by three additional observations. First, 2,3-dimethyl-2-butene, an alkene that is much more reactive than styrene in electrophilic additions,[5a] including the addition of arenesulfenyl[5a] and benzeneselenenyl[5b] chlorides, but much less reactive than styrene in free radical addition reactions,[5c] does not yield a photoadduct with **1**. Second, if an initial [1-hexene]/[**1**] ratio of 10:1 is employed, adducts $ArSO_2(CH_2\underset{Bu}{\underset{|}{C}}H)_xSePh$ were x > 1 are formed along with the 1:1 alkene-**1** adduct shown in Table I. Third, if the alkene used is 1,1-diphenylethylene, where the resonance stabilization by the two phenyl groups of the $ArSO_2CH_2\dot{C}Ph_2$ radical formed in eq 6a is apparently sufficient to make that radical too unreactive toward **1** for reaction 6b to proceed at a sufficiently rapid rate, one finds (a) that photodecomposition of **1** is retarded (reaction time, 12 hrs) and (b) that a major product is the unsaturated sulfone **3**[6] (0.33 mmol/mmol **1** decomposing), **3** is thought to be formed by the reaction sequence[7]

$$ArSO_2\cdot + CH_2{=}CPh_2 \longrightarrow ArSO_2CH_2\dot{C}Ph_2 \xrightarrow{PhSe\cdot} \underset{\textbf{3}}{ArSO_2CH{=}CPh_2} + \left[PhSeH\right]$$

Photoaddition of **1** (Ar = p-tolyl) to norbornadiene (eq 7) gives a 70% yield of a mixture of 1:1 adducts, consisting primarily (85-90%) of exo (**4a**) and endo-5-phenylseleno-exo-3-nortricyclyl p-tolyl sulfone (**4b**), but also containing a small amount (10-15%) of 3-phenylseleno-5-nobornen-2-yl p-tolyl sulfone (**5**).[9] The ratio of **5**/**4** is almost identical to that

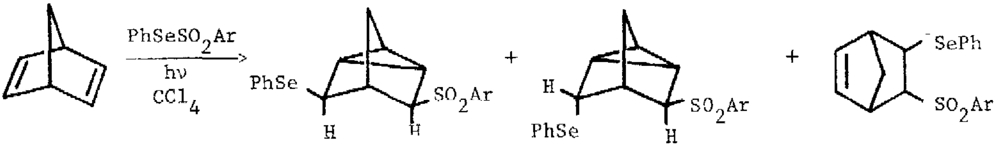
Table I

Photoaddition of p-Tolyl Benzeneselenosulfonate (1, Ar = p-Tolyl) to Simple Alkenes[a]

Alkene	Photoaddition product, 2, (yield), m p[b]	Product of elimination of selenoxide from oxidation of 2, (yield), m p.
CH_2=CH-Bu-n	 $ArSO_2CH_2\overset{Bu\text{-}n}{CH}SePh$ (66%), 53-56°C	 (62%), oil[c]
CH_2=CH-Ph	 $ArSO_2CH_2\overset{Ph}{CH}SePh$ (73%), 153-155°C	 (77%), 121-122°C[c]
	 (80%), 57-59°C	 (83%), 82-83°C[d]
$(CH_3)_2C=C(CH_3)_2$	No adduct formed	

(a) Photoadditions carried out by photolyzing a CCl_4 solution of 1 (0.3 M) and the alkene (0 3-0.6 M) in pyrex for 1 5 hr. in a Rayonet reactor (RPR-2537 lamp) (b) All adducts gave nmr, ir, and mass spectra consistent with assigned structures plus satisfactory C,H analyses. Structures confirmed by oxidation of 2 to corresponding selenoxide which then underwent elimination to give unsaturated sulfone shown in right hand column (c) The coupling constant (J = 15 Hz) for the two olefinic protons in this sulfone shows it to be the E-isomer (d) Ref 8

found by Cristol and Davies[10a] for the photoaddition of $PhSO_2Br$ to norbornadiene at similar dilution in chlorobenzene as solvent and indicates that the reactivity of 1 towards radicals in eq 6b is apparently very similar to that of $ArSO_2Br$. Cristol et al [10b] also report a ratio for exo-5-bromo to endo-5-bromo isomers (4 3) not greatly different from the ratio of 4a to 4b (7 6) found[11] for eq 7



4a 4b 5

(7)

Photoaddition of 1 to alkenes is much faster than the additions of 1 to the same substrates described by Back and Collins[2a] and Kobayashi and Miura.[2b] Where the two reactions give the same product (addition of 1 to cyclohexene, or to styrene in refluxing benzene or chloroform) photoaddition would therefore seem the method of choice for the synthesis of 2 Given the sensitivity of solutions of 1 to ordinary room light, one must also wonder whether photoaddition could be playing any role in some of the reactions thought[2] to be purely thermal processes. Reexamination of these reactions under conditions where the solution is shielded from light may therefore be warranted

References and Notes

(1) The research supported by the National Science Foundation, Grant CHE-79-18877

(2) (a) T. G. Back and S. Collins, *Tetrahedron Letters*, 2215 (1980) (b) M Kobayashi and T. Miura, *9th Int'l Symposium on Organic Sulfur Chemistry*, Riga, USSR, June, 1980, Abstracts, p 165.

(3) da Silva Correa and Waters[4] have shown that reaction of two $ArSO_2\cdot$ radicals leads to the formation of $ArS(O)OSO_2Ar$, and this mixed anhydride then breaks down immediately to give the sulfonic anhydride $ArSO_2OSO_2Ar$ and other product(s) In their system the other product was the thiolsulfonate $ArSO_2SAr$, but this is not found in the present case. Instead one has one or more rather unstable sulfur and selenium containing compounds that have so far resisted our efforts to isolate them in a pure form

(4) C. M M da Silva Correa and W A. Waters, *J Chem. Soc (D)*, 1874 (1968)

(5) (a) G H Schmid and T T. Tidwell, *J. Org Chem* , **43**, 460 (1978). (b) G. H Schmid and D. G Garratt, Chap 9 in "The Chemistry of Double Bonded Functional Groups," S Patai, ed , John Wiley and Sons, New York, 1977, p 856 (c) M Szwarc and J H Binks, "Theoretical Organic Chemistry," Kekule Symposium, 1958, Butterworth Scientific Publications, London, 1958, pp. 271, 272, 278.

(6) J. L Kice and N E Pawlowski, *J Am. Chem Soc* , **86**, 4498 (1964)

(7) That $ArSO_2CH_2CPh_2$ will undergo reaction with other radicals to give **3** has been shown.[6]

(8) F G Bordwell and R J. Kern, *J Am Chem. Soc* , **77**, 1141 (1955)

(9) The amount of **5** in the adduct mixture was determined by comparing the integrated intensity of the nmr signal for the two olefinic protons in **5** (δ 6 10-6.25) with that for all the aromatic protons (δ 7.0-8 0) in the adduct mixture

(10) (a) S J Cristol and D I Davies, *J Org Chem* , **29**, 1282 (1964). (b) S J. Cristol, J K Harrington, and H S. Singer, *J Am Chem Soc* , **88**, 1529 (1966)

(11) The ^{1}H-nmr spectrum of **4b** shows signals at δ 3 87 ($C\underline{H}SO_2Ar$) and 3 34 ($C\underline{H}SePh$) while that of **4a** shows signals for the same protons at δ 3 19 and 3 05. The ratio **4b**/**4a** in a mixture of the two can be determined from the relative integrated intensities of these signals The stereochemistry of the two 5-phenylseleno compounds was established by taking the corresponding *exo*-5-bromo and *endo*-5-bromo compounds (prepared from $ArSO_2Br$ and norbornadiene), whose stereochemistry can be unambiguously assigned by comparison of the locations of the nmr signals for the protons at C-3 and C-5 with those for the same protons in *exo* and *endo*-5-bromo-*exo*-3-nortricyclyl phenyl sulfones,[11b] and converting them by reaction with $PhSe^-$ (inversion of configuration at C-5) into **4b** and **4a**, respectively

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