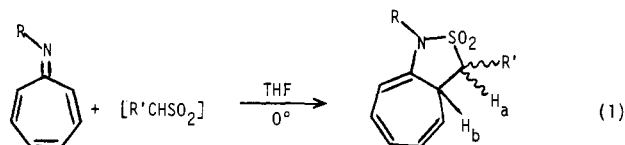


Stereoselective Cycloadditions of Sulphenes with 8-Azaheptafulvenes and Base-Induced Conversions of the Resulting Cycloadducts to (*Z*)- ω -Styrenesulfonamides

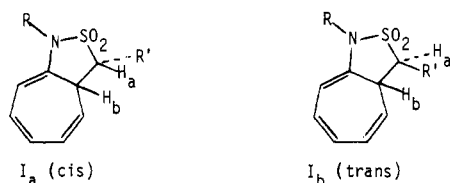
Sir:

Several years ago, stereoselective cycloadditions of sulfenes with tropone to form γ -sultones were reported.¹ Only sulfenes with electron-withdrawing substituents gave adducts, alkyl-sulfenes and sulfene itself being unreactive toward tropone. We now wish to report the stereoselective cycloadditions of several alkyl- and arylsulfenes, as well as simple sulfene, to 8-alkyl-8-azaheptafulvenes to form the corresponding γ -sultams (eq 1 and Table I).



Treatment of a suspension of the 8-alkyl-8-azaheptafulvenium tetrafluoroborate in anhydrous tetrahydrofuran with 2 equiv of triethylamine at 0 °C under nitrogen generated the corresponding azaheptafulvene.² A solution of the sulfonyl chloride in anhydrous tetrahydrofuran was then added dropwise (2–3 h) at 0 °C. The second equivalent of base generated the sulfene. Filtration of triethylamine hydrochloride and reduced-pressure removal of the solvent gave a dark brown oil, which was taken up in methylene chloride. The solution was washed with water and dried and the solvent evaporated to give the crude product, which was purified by recrystallization from absolute ethanol or by column chromatography on silica gel (CH₂Cl₂ eluent).

Structural assignments of the cycloadducts were made on the basis of their exact masses and IR and NMR spectra. All are consistent with one to one adducts (I_a or I_b) and are similar to those of the analogous γ -sultones.¹ In all cycloadditions only



one of the two geometrical isomers is obtained, and inspection of NMR spectra taken on the crude reaction mixtures indicates that isomerization does not take place during purification.

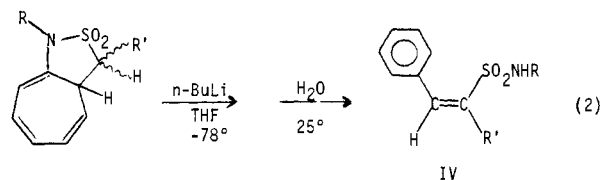
The initial adducts are converted to their geometric isomers in excellent to quantitative yields by treatment with *n*-butyllithium at –78 °C in tetrahydrofuran followed by quenching of the resulting α -sulfonyl carbanion at the same temperature. Each member of an isomer pair exhibits similar IR and NMR

spectra and nearly identical mass spectra. Comparison of the chemical shifts of H_a and H_b for each isomer pair with the corresponding values for the analogous γ -sultones¹ suggests that the initial adducts are the *cis* isomers (I_a).³

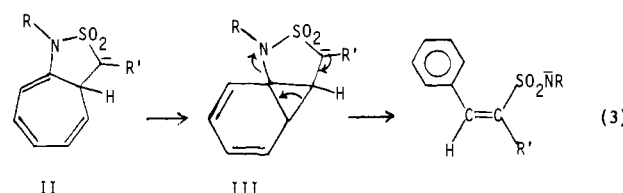
The assignment of *cis* geometry to the initial γ -sultams is supported by the fact that the isomerization of the initial methylsulfene adducts gives an equilibrium mixture containing 85–90% *trans* isomer. Models confirm the greater steric strain present in the *cis* isomer. Isomerization was complete for all of the other cycloadducts.

The *cis* selectivity of these cycloadditions is remarkable. Although reminiscent of sulfene–tropone cycloadditions, there the sulfenes bore substituents capable of electron delocalization and/or secondary orbital interactions, which could account for the observed *cis* selectivity.¹ However, most of the sulfenes that have been added to the 8-azaheptafulvenes have contained alkyl substituents. Possibly there is weak, long-range attraction between the alkyl substituent on the sulfene and the ring system of the azaheptafulvene favoring an *endo*-oriented dipolar transition state.

When the intermediate α -sulfonyl carbanions (II) in the isomerization reactions are allowed to warm to room temperature before quenching an interesting rearrangement takes place (eq 2). The products of this rearrangement have been identified as ω -styrenesulfonamides (IV).⁴ The same styrene



derivative is obtained, regardless of whether the anion is generated from the *cis*- or *trans*- γ -sultam. Presumably the anion, when warmed, undergoes a thermally allowed disrotatory ring closure to a norcaradiene structure (III). A six-electron shift produces the sulfonamide anion (eq 3), which is protonated



subsequently. This mechanism is analogous to that proposed by Doering and Denney for the alkali-induced conversion of 2-halotropones to benzoic acid.⁵

The only γ -sultam that failed to undergo this rearrangement is the adduct from sulfene and 8-methyl-8-azaheptafulvene. Refluxing the anion from that adduct in tetrahydrofuran for 1 h did not effect rearrangement. Apparently the presence of a substituent on the α -sulfonyl carbon is a necessary factor in

Table I

R	R'	Mp, °C, <i>cis</i>	Yield, ^a %	Mp, °C, <i>trans</i>	Yield, ^b %	Chemical shift, δ			
						H _a , <i>cis</i>	H _a , <i>trans</i>	H _b , <i>cis</i>	H _b , <i>trans</i>
CH ₃	H ^c	74–76	32			3.74	3.36		2.95
CH ₃ CH ₂	H ^c	Oil	75			3.68	3.30		2.80
CH ₃	CH ₃	113–113.5	70	Oil	94 ^d	3.65	3.48	2.70	2.55
CH ₃ CH ₂	CH ₃	92–93	84	Oil	95 ^e	3.65	3.50	2.63	2.55
CH ₃	CH ₃ CH ₂	106–107	63	Oil	91	3.50	3.30	2.60	2.54
CH ₃	(CH ₃) ₃ C	90–91	47	115–118	94	3.43	3.37	2.48	2.65
CH ₃	C ₆ H ₅	173–175	68	138–141	100	4.81	4.55	3.34	3.12
CH ₃ CH ₂	C ₆ H ₅	134–135	73	128–129.5	100	4.78	4.51	3.25	3.17

^a For initial adducts, after purification. ^b For isomerized adducts, after purification. ^c No geometric isomers. ^d A mixture of 85% *trans*, 15% *cis*. ^e A mixture of 90% *trans*, 10% *cis*.

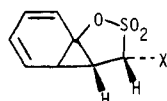
the process. The methylsulfene-8-methyl-8-azaheptafulvene cycloadduct underwent only partial rearrangement at room temperature, with the isolated product being identified as a 3:1 mixture of the (*Z*)- ω -styrenesulfonamide and *trans*- γ -sultam. All other γ -sultams rearranged completely to give excellent to quantitative yields of (*Z*)- ω -styrenesulfonamides.

In contrast to the γ -sultones, the γ -sultams are relatively thermally stable. The γ -sultones, when refluxed in dioxane for 1 h, lost sulfur dioxide and rearranged to give 2-hydroxystilbenes and styrenes.¹ Attempted thermolysis of several of these γ -sultams (both *cis* and *trans* isomers) failed, even when more vigorous conditions were used (145 °C in dimethylformamide for 20 h).

Further studies of this cycloaddition reaction and the interesting rearrangement of the resulting γ -sultams are underway and will be reported at a later date.

References and Notes

- (1) W. E. Truce and C. M. Lin, *J. Am. Chem. Soc.*, **95**, 4426 (1973). There is a typographical error in formulas IVa and IVb in that publication; the correct respective formulas are



and the corresponding *trans* structure.

- (2) N. L. Bauld and Y. S. Rim, *J. Am. Chem. Soc.*, **89**, 6763 (1967).
- (3) The chemical shifts of H_a and H_b in the *cis* isomers generally appear further downfield than in the *trans* isomers.
- (4) The structural assignments for the sulfonamides were supported unambiguously by their NMR, IR, and mass spectra. Recently the phenylsulfene-tropone cycloadduct has been similarly rearranged to give *trans*-1,2-diphenylethanesulfonic acid (unpublished results from this laboratory).
- (5) W. von E. Doering and D. B. Denney, *J. Am. Chem. Soc.*, **77**, 4619 (1955).

William E. Truce,* James P. Shepherd

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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Time Independent Diffusion Controlled Reaction Rate Constants

Sir:

In this communication we report the observation of second-order reactions in the solid state that are diffusion controlled with a constant rate constant at all times; in other words reactions which follow accurately the following equation.

$$1/c - 1/c_0 = kt^{1/2} \quad (1)$$

Based on the so-called Smoluchowski¹ boundary condition Waite² some time ago derived the following equation

$$\frac{1}{c} - \frac{1}{c_0} = \kappa \left[1 + \frac{2r_0}{(\pi Dt)^{1/2}} \right] t \quad (2)$$

for the second-order rate of a diffusion controlled reaction between like species where c is the concentration at time t , c_0 the initial concentration at zero time, κ is a constant equal to $4\pi r_0 D$, D is the sum of the diffusion coefficients of the individual reacting species, and r_0 is the free-radical separation distance within which they react and outside of which the potential of an unreacted radical is independent of position (Smoluchowski boundary condition). The radius r_0 may be considered to be the radius of the reaction cage. As shown before by us³ eq 2 can be converted to a linear form

$$\left(\frac{1}{c} - \frac{1}{c_0} \right) \frac{1}{t^{1/2}} = \kappa t^{1/2} + \frac{2r_0\kappa}{(\pi D)^{1/2}} \quad (3)$$

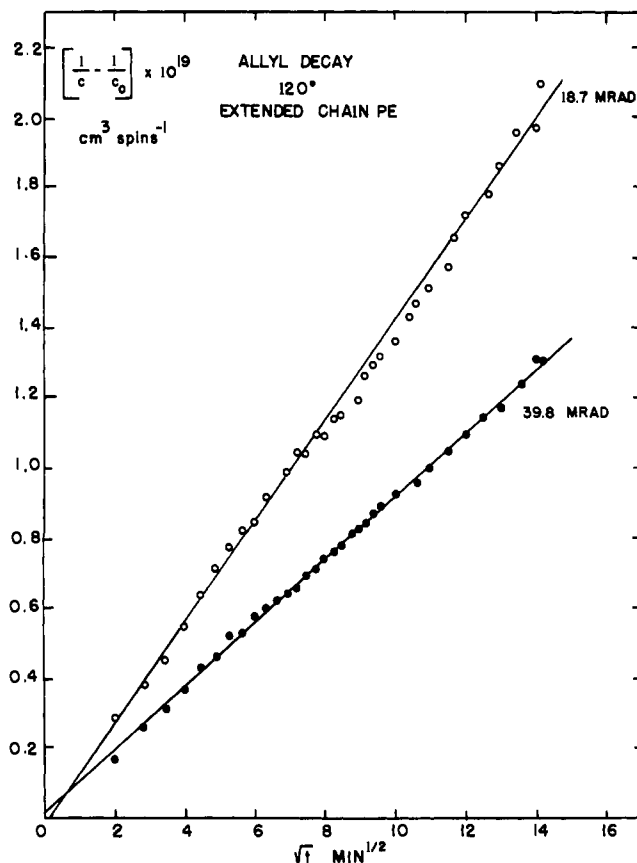


Figure 1. Chain allyl free-radical decay in vacuo at 120 °C in extended chain polyethylene irradiated to doses of 18.7 Mrad (open circles) and of 39.8 Mrad (solid circles) at 77 K. Solid lines represent a least-squares fit of eq 1 to the data.

so that by plotting the left-hand side of eq 3 as a function of $t^{1/2}$ it can be readily seen whether a linear relation is obtained and more importantly whether $(1/c - 1/c_0)/t^{1/2}$ extrapolates to a finite intercept at time t equal to zero in which case the reaction is diffusion controlled. An ordinary second-order reaction would give a zero intercept.

The term $2r_0/(\pi Dt)^{1/2}$ inside the brackets of eq 2 will usually be negligible with respect to unity because in most liquid systems D will be of the order 10^{-6} cm²/s and $r_0 \sim 10^{-7}$ cm, but, if the reaction occurs in times of the order of micro- or nano-seconds, then $2r_0/(\pi Dt)^{1/2}$ will no longer be negligible and the reaction becomes diffusion controlled. However, if the diffusion constant is orders of magnitude smaller than 10^{-6} cm²/s as in reactions occurring in the solid state, there is the possibility that the term $2r_0/(\pi Dt)^{1/2}$ of eq 2 may be much greater than unity at all times up to 100 min, for example. For unity being only 10% of $2r_0/(\pi Dt)^{1/2}$ at t equal to 100 min or 6×10^3 s, it is necessary that r_0 be as large as 4×10^{-7} cm and D as small as 3.4×10^{-19} cm²/s. If unity can be neglected in eq 2, then we obtain eq 1 in which

$$k = [2r_0\kappa/(\pi D)^{1/2}] = 8r_0^2(\pi D)^{1/2} \quad (4)$$

We call such situations reactions with "time independent diffusion controlled reaction rate constants".

As an example of the applicability of eq 1 to a solid-state reaction, we have plotted in Figure 1 data for the decay of the allyl free radical at 120 °C in samples of extended chain (98% crystalline) polyethylene irradiated in vacuo to 18.7 and 39.8 Mrad, respectively, at 77 K and then heated to 120 °C in vacuo to observe the allyl radical recombination reaction. Over the time period illustrated ~20% of the allyl radicals decayed. Equation 1 is accurately followed with intercepts at zero time determined by the least-squares method equal to -0.019 and