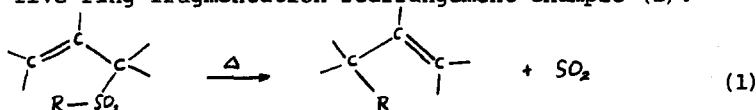


A NEW THERMAL PERICYCLIC CARBON TRANSFER
CAPABLE OF CREATING QUATERNARY SITES

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A recent systematic analysis of the variety of thermal pericyclic reactions with respect to variations in the involved atoms¹ has led to an approach for inventing new synthetic construction² reactions. We have applied this to a predicted five-ring fragmentation-rearrangement example (1).



The allyl sulfones are easily synthesized by the displacement reaction of alkane- (or arene-) sulfinates with various allyl bromides³ in 1:1 dioxane-water at room temperature (8 hours); the sulfinates were easily created in turn by bubbling sulfur dioxide into alkyl or aryl lithium solutions and filtering the precipitated salts. The liquid sulfones were distilled in vacuo and characterized as pure materials by tlc (in several chloroform-hexane solvent mixtures) and ir and nmr spectra. The sulfones prepared, with no optimization of yield, are listed in Table I.

Table I. Formation and Pyrolysis of Allyl Sulfones

R-SO ₂ :Li ⁺	Bromide	(yield)	Pyrolysis product	(yield) ^a
t-Butyl	allyl (CH ₃) ₃ CSO ₂ CH ₂ CH=CH ₂	(73%)	(CH ₃) ₃ C-CH ₂ CH=CH ₂	(80%)
	crotyl (CH ₃) ₃ CSO ₂ CH ₂ CH=CHCH ₃	(72%)	tars/300°	
	cinnamyl (CH ₃) ₃ CSO ₂ CH ₂ CH=CHC ₆ H ₅	(82%)	tars/300°	
n-Butyl	allyl CH ₃ (CH ₂) ₃ SO ₂ CH ₂ CH=CH ₂	(70%)	CH ₃ (CH ₂) ₃ -CH ₂ CH=CH ₂	(34%)
	crotyl CH ₃ (CH ₂) ₃ SO ₂ CH ₂ CH=CHCH ₃	(68%)	CH ₃ (CH ₂) ₃ -CH(CH ₃)CH=CH ₂	(>10%)
p-Tolyl	allyl p-CH ₃ C ₆ H ₄ SO ₂ CH ₂ CH=CH ₂	(78%)	p-CH ₃ C ₆ H ₄ -CH ₂ CH=CH ₂	(53%)

^a Products were analyzed by glc and nmr comparison with authentic compounds. Yields by glc (toluene as internal standard) on a 12 ft. 5% S.E.-30 column.

Pyrolysis of t-butyl allyl sulfone at 290° for 15 minutes (optimum conditions) in a sealed tube led to sulfur dioxide and an 80% yield of

4,4-dimethyl-1-pentene, identified by glc and nmr comparison with an authentic sample. The fact that the sulfone was entirely in the gas phase at 290° when reaction occurred supports the presumption of a concerted thermal reaction. The isomerized sulfone, $(\text{CH}_3)_3\text{CSO}_2\text{CH}=\text{CHCH}_3$ ($\lambda_{\text{max}} 255 \text{ nm}$), was formed by stirring t-butyl allyl sulfone with potassium carbonate/acetone 6 hours at room temperature. As anticipated from equation (1), this isomer undergoes no reaction on pyrolysis below 400°, at which temperature only tars are formed.

The other examples shown in Table I were pyrolyzed by syringe injection into a heated tube (1 x 30 cm) filled with quartz beads and the products collected in a cold trap; they generally required higher temperatures (350-400°) although temperature (and yield) optimization was not undertaken for these examples. The reaction proceeded as well with the p-tolyl sulfone, implying that carbonium ion character at the transferred carbon is not a feature of the mechanism. The relative ease (lower temperature) of the t-butyl case suggests some steric facilitation of the carbon-sulfur bond cleavage but increased substitution of the allyl component appears to block the carbon transfer in the two other t-butyl sulfones which produced only tars at 300°.

The reaction belongs to an important synthetic class which constructs carbon-carbon single bonds by simple thermolysis; the present example adds not only a potentially useful method to the small collection of synthetic reactions capable of producing quaternary carbons but also a new way of converting an aromatic sulfonyl substituent to an alkyl one.⁴ At present nothing is known of the stereochemistry of bond formation, although the presumptive pericyclic pathway implies a parallel with the stereochemistry of other 2,3-sigmatropic rearrangements.⁵

References

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