

sion of 7 (Ar = Ph) and a 0.2 molar equiv of phosphorus pentasulfide was heated under reflux in pyridine for 1 hr and poured through filter paper into a large volume of warm (50°) water.⁴ The thioamide 8 (Ar = Ph), mp 163-165°, obtained in quantitative yield, was heated with methyl iodide in tetrahydrofuran solution; the product was neutralized with triethylamine, extracted with dichloromethane, and purified by distillation to give the desired thioimidate (9, Ar = Ph), 68%, mp 94-95°. Several other members of this series were prepared in an analogous manner with yields of 33, 50, and 60% for 9b, 9c, and 9d, respectively.

The reaction of 9a with methoxyacetyl chloride and triethylamine in dichloromethane gave a single product, ir (Nujol) 1780 cm⁻¹, mp 73-74°, in 68% yield, which was shown to be the bicyclic β -lactam 10 on the basis of ir, mass spectral and pmr characteristics.



The stereochemistry of the β -lactam 10 was established by studying the pmr spectrum of the sulfoxide, 11, mp 122-123°, and the sulfone 12, mp 145-146°, obtained by successive oxidations of 10a with *m*-chloroperoxybenzoic acid.⁵ The sulfur was confirmed to be the site of oxidation by the progressive downfield shift of the methylthio group in the pmr spectrum, going from 2.20 ppm in 10a to 2.45 ppm in 11 to 3.17 ppm in 12. For this series of compounds



the methoxyl resonance position was virtually unchanged while the C-6 proton shifted from 4.41 ppm in 10 to 4.68 ppm in 11 and 4.60 ppm in 12.

The 16-Hz anisotropic deshielding effect observed for the C-6 proton upon oxidation of the C-5 methythio substituent is clearly appropriate only for a situation in which the methythio group is oriented cis to the C-6 proton and thus trans to the C-6 methoxy group. In all of these compounds the olefinic proton showed a characteristic trans allylic coupling of 1-2 Hz. On the basis of the pmr data the stereostructure 10a can be deduced. The trans disposition of the methoxy group in 10a with respect to the thio function is in agreement with the directive influence and stereospecificity observed earlier by us in forming β -lactams from thioimidates.⁶ In view of our earlier studies on the cycloaddition of various acid chlorides-in particular azidoacetyl chloride-to imines, it can be expected that the method described above could be extended to the synthesis of diverse bicyclic β -lactams of type 2. Further work along these lines is in progress.

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References and Notes

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Department of Chemistry and	Ajay K. Bose*
Chemical Engineering	John L. Fahey
Stevens Institute of Technology	
Hoboken, New Jersey 07030	

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Thermal Rearrangement of 1,2-Epoxyethylbenzene

Summary: Thermolysis of 1,2-epoxyethylbenzene at 500° has been found to produce toluene while thermal rearrangement at 200-300° gives phenylethanal via a firstorder process; $k = 6.02 \pm 0.12 \times 10^{-2} \text{ hr}^{-1}$ at 200° in benzene.

Sir: We wish to communicate the results of our investigation of the thermal lability of 1,2-epoxyethylbenzene (1). While subjection of 1 to temperatures in the range of 500° leads to a clean thermolysis to toluene (2) (Figure 1) and, presumably, carbon monoxide with traces of phenyl acetylene ($\sim 1.6\%$) also being formed, the use of more moderate temperatures gives selective rearrangement of 1 to phenylethanal (3) via epoxide ring opening and a formal 1,2hydrogen shift.



Rate data, obtained under liquid phase conditions in benzene solution, show this rearrangement to obey firstorder kinetics and to have rate constants as tabulated in Table I. Activation parameters derived from these data are $E_a = 29.2 \pm 0.6 \text{ kcal/mol}, \Delta H^*_{200} = 28.3 \pm 0.6 \text{ kcal/}$ mol, and $\Delta S^*_{200} = +11.0 \pm 1.2 \text{ cal/mol}^\circ \text{K}$. In addition, the rate of rearrangement appears to be somewhat influenced by solvent, being $\sim 35\%$ more rapid in benzene (at 200°) than in toluene.

The dramatic influence of the phenyl substituent on the direction of ring opening of 1 is demonstrated by the absence of acetophenone (6) from the product mixture. This contrasts markedly with the complete lack of selectivity in C1-O vs. C2-O bond breakage reported by Gritter and Sabatino¹ for the photolysis of 1 at 2537 Å. A rather selec-



Figure 1. Vapor-phase thermolysis of 1,2-epoxyethylbenzene at 500°: •, 1,2-epoxyethylbenzene, \blacktriangle , toluene.

tive conversion of 1 to 3 (85%) accompanied by 6 (4%) in the presence of sodium iodide-n-propyl iodide-dimethyl sulfoxide has been previously reported² as has the isomerization of 1 to 3 (no yield given) in the presence of $LiClO_4$ ³ but, to our knowledge, ours is the first report of the thermally induced conversion of 1 to 3.

The selectivity of aldehyde formation herein and the positive ΔS^* observed constitute evidence for either a diradical or ionic mechanism involving intermediate 4 or 5, respectively. While both 4 and 5 are benzylically stabilized, neither of the corresponding intermediates, 4' nor 5', leading to acetophenone (6) benefit from such stabiliza-



tion. The selectivity to aldehyde could also be rationalized on the basis of a concerted mechanism $(1 \rightarrow 7 \rightarrow 3)$ as benzylic C-O bond breakage requires less energy than does



cleavage of the bond linking the primary carbon to oxygen,⁴ and the transition state for the rearrangement more closely resembles reactant 1 than product 3 owing to the exothermic nature of the reaction. However, any influence of product (3 and 6) stability on the transition state would weigh in favor of ketone 6 formation, because, of the transition states (7 and 7', respectively) leading to aldehyde 3 and ketone 6 formation, the latter should be favored owing to the developing conjugation between the carbonyl and phenyl moieties. This fact plus the observed positive ΔS^* lead the authors to favor the stepwise mechanism at this time. Finally, it should be noted that the present evidence does not preclude the possibility of aldehyde formation via C₂-O bond scission with phenyl migration as opposed to

Table I First-Order Rate Constants. Rearrangement of 1,2-Epoxyethylbenzene to Phenylethanal

Temp, °C	k, hr^{-1}
180 200 220	$egin{array}{c} 1.32 \pm 0.04 imes 10^{-2} \ 6.02 \pm 0.12 imes 10^{-2} \ 1.86 \pm 0.03 imes 10^{-1} \end{array}$

the above depicted C1-O bond scission-hydrogen migration sequence.

Rearrangements at 500° were conducted using $50-\mu l$ samples of 1 sealed in vacuo in Pyrex tubes; those at the lower temperatures were run using both neat samples of 1 in sealed tubes and benzene or toluene solutions thereof in a stirred stainless steel reactor. Substantial polymerization was observed upon thermolysis in sealed tubes (unseasoned) at 200°, but rearrangements of 8:1 benzene or toluene solutions of 1 consistently provided yields of 91-96% of the aldehyde. Extent of rearrangement was monitored by glc; product identities were confirmed by glc and spectroscopic comparisons with authentic materials. The rates and activation parameters reported were subjected to least-squares optimization; the uncertainties in k are probable errors while those in the values of the activation parameters are statistical errors determined by the method of Purlee.⁵

Experimentation, the purpose of which is to further elucidate the mechanism and scope of this rearrangement, is continuing.

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Cosden Oil and Chemical Company James M. Watson* Big Spring, Texas 79720 Bernard L. Young

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Structure of the Products Resulting from Photochemically Induced Hydrogen Transfers in the Levopimaric Acid-Cyclopentenedione Adduct

Summary: X-Ray analysis of a derivative of the substance obtained by irradiation of the levopimaric acid-cyclopentenedione adduct confirms that the unusual series of photochemical reactions leading to its formation involves intramolecular energy transfer from enone to isolated double bond and two consecutive transannular hydrogen abstractions, each accompanied by ring closure.

Sir: In attempting to establish the stereochemistry of the levopimaric acid-1-cyclopentene-3,5-dione adduct la,¹ we observed a remarkable example of intramolecular energy transfer which also had important implications for cyclopentenone photochemistry. Irradiation of 1b afforded not only the expected cage structure, but also, by transfer of excitation energy from triplet cyclopentenone to the isolated double bond, an isomer A which was formulated as