

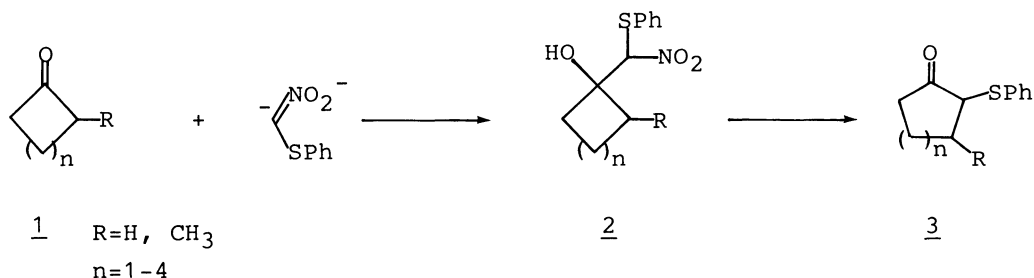
A Ring Expansion of Cyclic Ketones to  $\alpha$ -Phenylthio Ketones  
via Lewis Acid Mediated Denitration

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The adducts of cyclic ketones with the lithium derivative of (phenylthio)nitromethane are readily rearranged to the ring expanded  $\alpha$ -phenylthio ketones via aluminum chloride mediated denitration.

The importance of a nitro group as an anion stabilizing substituent in carbon-carbon bond formation reactions are well recognized in organic synthesis.<sup>1)</sup> The nitro group, which is bonded to the carbon bearing carbocation stabilizing substituents, has been recently reported to act as a leaving group in the presence of Lewis acids.<sup>2)</sup>



On the basis of the unique feature of a nitro group, we have found that (phenylthio)nitromethane<sup>3,4)</sup> can serve as a useful one carbon and  $\alpha$ -heteroatom source in ring expansion of cyclic ketones.<sup>5)</sup> The  $\alpha,\alpha$ -doubly deprotonated dianion of (phenylthio)nitromethane, generated with 2.0 equiv. of *n*-butyllithium in THF and HMPA (5:1) at  $-80^\circ\text{C}$ , was readily added to cycloalkanones at  $-80^\circ\text{C}$  within 1 h except for cyclopentanone.<sup>6)</sup> In the case of cyclopentanone, trimethylsilyl enol ether of cyclopentanone was obtained as a major product after quenching with trimethylsilyl chloride and the addition of diethylaluminum chloride, magnesium bromide, and ceric chloride did not improve the reaction. Subsequent rearrangement of the adducts<sup>7)</sup> was attempted with various Lewis acids such as diethylaluminum chloride, aluminum chloride, stannic chloride, and titanium tetrachloride. Among them aluminum chloride gave the best results and is generally recommended. The rearrangements of 4-, 5-, and 6-ring adducts proceeded readily with 2.0 equiv of aluminum chloride in dichloromethane at  $0^\circ\text{C}$  for 30 min to produce ring expanded  $\alpha$ -phenylthio ketones,<sup>5,8)</sup> whereas somewhat low efficiency was observed with the 7-ring adducts.

Table 1. Ring Expansion of Cyclic Ketones to  $\alpha$ -Phenylthio Ketones

Ketone	Yield of <u>2</u> <sup>a)</sup>	Yield of <u>3</u> <sup>b)</sup>
	%	%
3-Phenylcyclobutanone	78	66
2-Methyl-3-phenylcyclobutanone	85	74
Cyclopentanone	31 <sup>b)</sup>	92
Cyclohexanone	92	68
2-Methylcyclohexanone	83	78
Cycloheptanone	73	41
2-Methylcycloheptanone	52	63

a) Crude yields. b) Isolated yields.

For unsymmetrical ketones, the most highly substituted alkyl group migrates preferentially. Thus, the rearrangement of the adducts from 2-methylcyclohexanone and 2-methylcycloheptanone reveals a 98:2 preference for the migration of the most substituted alkyl group, respectively, which was determined by Birch reduction of the isomeric mixture and the following GLC analysis.

The present method for a ring expansion is another example of the dual property of the nitro compounds, i.e., to be nucleophiles in the presence of bases and to be electrophiles in the presence of Lewis acids and this unique property of a nitro group appears to provide many useful applications in organic synthesis.

#### References

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- 5) The similar ring expansion reaction using PhSCH<sub>2</sub>SO<sub>2</sub>Ph was reported during our study. B. M. Trost and G. K. Mikhail, *J. Am. Chem. Soc.*, **109**, 4124 (1987).
- 6) Reaction of cyclopentanone with the monanion of PhSCH<sub>2</sub>NO<sub>2</sub> did not occur.
- 7) Most addition products were unstable, showing high propensity for dehydration and retroaldol type of the reaction on a silica gel column.
- 8) For a ring expansion to  $\alpha$ -phenylthio ketones, see: T. Cohen, D. Kuhn, and J. R. Falck, *J. Am. Chem. Soc.*, **97**, 4749 (1975); W. D. Abraham, M. Bhupathy, and T. Cohen, *Tetrahedron Lett.*, **1987**, 2203.

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