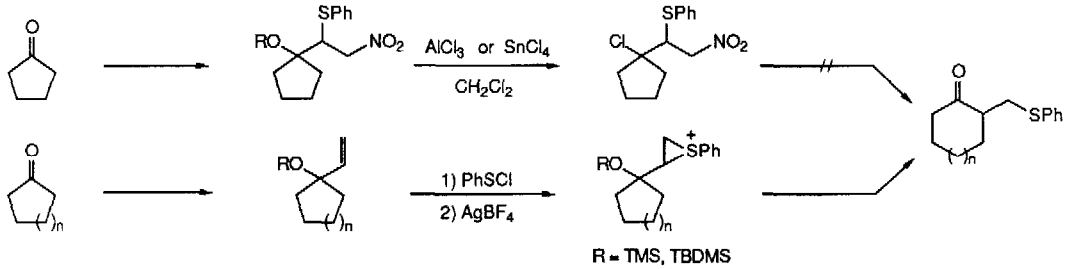
Tetrahedron Letters,Vol.30,No.45,pp 6181-6184,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

AN EPISULFONIUM ION MEDIATED RING EXPANSION OF 1-ALKENYLCYCLOALKANOLS†

Sunggak Kim* and Jung Ho Park
Department of Chemistry
Korea Advanced Institute of Science & Technology, Seoul 130-012, Korea

Summary : It has been found that TBDMS ethers of 1-alkenylcycloalkanols are readily rearranged to the ring expanded α-(1-phenylthioalkyl)cycloalkanones in high yields via episulfonium ions.

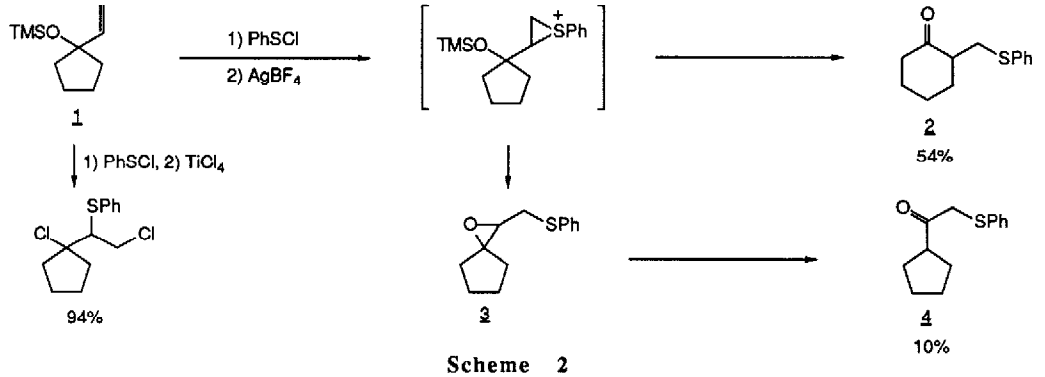
The importance of ring expansion methods in organic synthesis has been well recognized.[1] Much effort has been made to improve existing methods and to develope new ones, especially having the ability to introduce a heteroatom substituent together with the ring expansion.[2] Recently, we have reported that (phenylthio)nitromethane can serve as a useful one carbon and α-heteroatom source in the alkylidenesulfonium ion mediated ring expansion.[3] We have examined the possibility of a ring expansion via an episulfonium ion[4] using β-nitroethyl phenyl sulfide,[5,6] as shown in Scheme 1. However, this approach failed to give the ring expanded ketones by treatment with various Lewis acids such as aluminum chloride and stannic chloride. In all cases, the corresponding tertiary halides were obtained in high yields.



Scheme 1

We have found that t-butyldimethylsilyl (TBDMS) ethers of 1-alkenylcycloalkanols,[7] upon successive treatment with PhSCl and $AgBF_4$ gave the ring expanded α-(1-phenylthioalkyl)cycloalkanones[8] in high yields. 1-Alkenylcycloalkanols were easily prepared from cycloalkanols and vinyl magnesium bromide in tetrahydrofuran in high yields. The preliminary study was done

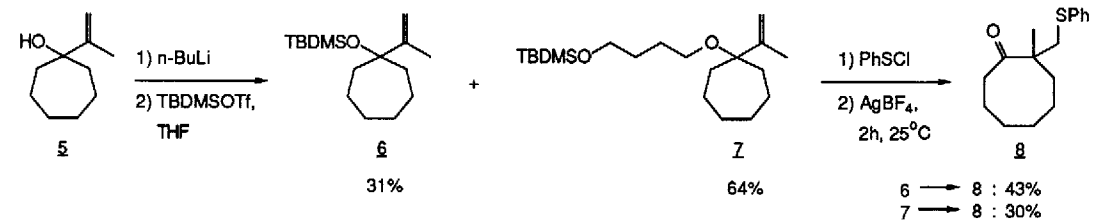
†Dedicated to professor G. Just on the occasion of his 60th birthday.



Scheme 2

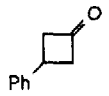
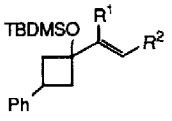
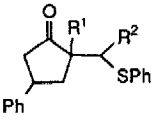
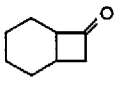
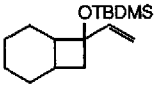
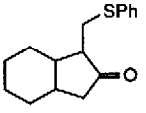
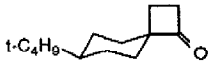
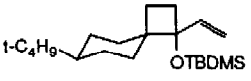
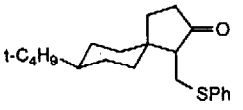
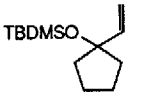
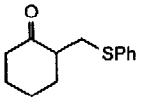
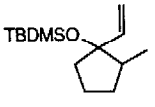
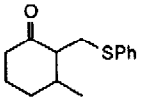
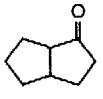
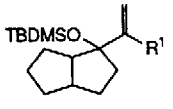
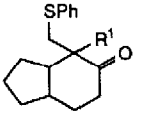
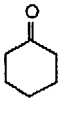
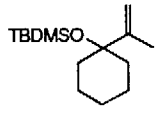
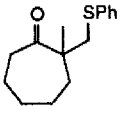
with trimethylsilyl (TMS) ether (1) using several binary systems, which has been known to generate an episulfonium ion from the double bond.[9,10] Among several reagent systems tested in this study,[11] $PhSCl/AgBF_4$ gave the best result, although it gave the undesired byproduct (4) derived from the rearrangement of the epoxide (3),[12] as shown in Scheme 2. The side reaction was completely suppressed by introducing TBDMS group. Thus, the ring expansion of the corresponding TBDMS ether proceeded cleanly, yielding α-(phenylthiomethyl)cyclohexanone (2) in 80% yield.

The silylation of 1-alkenylcycloalkanols was normally carried out with 1.5 equiv of TBDMSOTf and 2.5 equiv of 2,6-lutidine in dichloromethane at room temperature[13] and the TBDMS ethers were isolated in high yields, as shown in Table 1. However, this method reaches a limit with 1-isopropenylcycloheptanol (5). Under the present condition, the dehydrated diene was obtained as a major product along with a small amount of the TBDMS ether (6) probably due to the acidic environment. Thus, generation of an alkoxide with n-BuLi and treatment with TBDMSOTf gave the desired TBDMS ether (6) in 31% yield along with 64% of the tetrahydrofuran insertion adduct (7), as shown in Scheme 3. The use of other solvents such as dimethoxyethane, ether and hexane gave no improvement in the yield of the desired TBDMS ether.



Scheme 3

Table 1. Ring Expansions of cycloalkanones to α-(1-Phenylthioalkyl) Ketones[a]

ketone	substrate (yield, %[b])	temp, °C / time, h	product[c]	yield, %[d]
				
	$R^1 = R^2 = H$ (91)	0 / 1.5		98
	$R^1 = CH_3$, $R^2 = H$ (85)	0 / 1		94
	$R^1 = H$, $R^2 = CH_3$ (69)	-10 / 1.5		83
	 (87)	0 / 1		96[e]
	 (77)	0 / 1		84[e]
	 (62)	0 / 1		80
	 (56)	0 / 2		87[f]
				
	$R^1 = H$ (75)	0 / 1		85[e]
	$R^1 = CH_3$ (65)	-10 / 1		89[e]
	 (55)	25 / 2		58

[a]All reactions were carried out in CH_2Cl_2 by successive treatment with 1.0 equiv of benzenesulfenyl chloride (1.0 M in CH_2Cl_2) at -78°C and1.5 equiv of silver tetrafluoroborate (1.0 M in CH_3NO_2) at -40°C, and stirring under given conditions. [b]Overall yield for isolated product from starting ketone. [c]The stereochemical outcome of the products has not been fully determined. [d]Yields are based on TBDMS ethers of 1-alkenylcycloalkanols. [e]Pure regioisomer by ^1H NMR. [f]Mixture of regioisomers (97:3) by GLC analysis after Raney nickel desulfurization.

The ring expansion reaction was performed on various structurally different TBDMS ethers of 1-alkenylcycloalkanols using $PhSCl/AgBF_4$. Table 1 summarizes our experimental results and illustrates the efficiency, applicability, and scope of the present method. The 4- and 5-ring adducts are cleanly rearranged to the ring expanded α-(1-phenylthioalkyl)cycloalkanones in high yields irrespective of the substitution at double bonds and carbocyclic rings, whereas somewhat low efficiency was observed with the 6-ring adduct. It is noteworthy that the compound (7) underwent a ring expansion with much less efficiency. For unsymmetrical ketones, the most highly substituted alkyl group migrated preferentially.[14]

References and Notes

1. For reviews, see: C. D. Gutsche and D. Redmore, "Carbocyclic Ring expansion reactions, " Academic, New York (1968); P. A. S. Smith and D. R. Baer, *Org. React.*, **11**, 157 (1960).
2. W. D. Abraham, M. Bhupathy and T. Cohen, *Tetrahedron Lett.*, 2203 (1987); L. S. Liebeskind, D. Mitchell and B. S. Foster, *J. Am. Chem. Soc.*, **109**, 7910 (1987); B. M. Trost and G. K. Mikhail, *ibid.*, **109**, 4124 (1987) and references cited therein.
3. S. Kim and J. H. Park, *Chem. Lett.*, 1323 (1988).
4. The ring expansion of 1-vinylcyclopropanol to cyclobutanone with PhSeBr has been reported. B. M. Trost, J. K. Balkovec and M. K-T. Mao, *J. Am. Chem. Soc.*, **105**, 6755 (1983).
5. N. Ono, A. Kamimura, H. Sasatani and A. Kaji, *J. Org. Chem.*, **52**, 4133 (1987); N. Ono, T. Hashimoto, T. X. Jun and A. Kaji, *Tetrahedron Lett.*, 2277 (1987).
6. S. Ranganathan, D. Ranganathan and S. K. Singh, *Tetrahedron Lett.*, 2893 (1987); D. Seebach, R. Hennig, F. Rehr and J. Gonnerman, *ibid.*, 1161 (1977).
7. For ring expansions of 1-alkenylcycloalkanols, see: G. R. Clark and S. Thiensathit, *Tetrahedron Lett.*, 2503 (1985); P. M. Herrinton, M. H. Hopkins, P. Mishra, M. J. Brown and L. E. Overman, *J. Org. Chem.*, **52**, 3711 (1987); C. R. Johnson, C. J. Cheer and D. S. Goldsmith, *ibid.*, **29**, 3320 (1964).
8. K. Suzuki and M. Sekiya, *Syn. Commun.*, 297 (1981); I. Paterson and I. Fleming, *Tetrahedron Lett.*, 2179 (1979).
9. The addition of PhSCl gave the addition product without ring expansion.
10. E. D. Edstrom and T. Livinghouse, *J. Am. Chem. Soc.*, **108**, 1334 (1986); Y. Ito and T. Ogawa, *Tetrahedron Lett.*, 2723 (1987); R. P. Alexander and I. Paterson, *ibid.*, 5911 (1983); M. A. Ibrazimov and W. A. Smit, *ibid.*, 961 (1983); W. A. Smit, M. Z. Krimer and E. A. Vorob'eva, *ibid.*, 2451 (1975).
11. $PhSCl/ZnBr_2$ or AgOTf and $PhSOMe/BF_3 \cdot OEt_2$ or TMSOTf have been used but they were much less effective than $PhSCl/AgBF_4$.
12. R. J. Israel and R. K. Murray, Jr., *J. Org. Chem.*, **50**, 1573 (1985); S. Knapp, A. F. Trope, M. S. Theodore, N. Hirata and J. J. Barch, *ibid.*, **49**, 608 (1984); T. Cohen, D. Kuhn and J. R. Falck, *J. Am. Chem. Soc.*, **97**, 4749 (1975).
13. E. J. Corey, H. Cho, C. Rucker and D. H. Hua, *Tetrahedron Lett.*, 3455 (1981).

14. We gratefully acknowledge financial support from KAIST.

(Received in Japan 3 July 1989)