CHEMISTRY LETTERS, pp. 587-590, 1982.

SYNTHESIS OF VICINALLY SUBSTITUTED CYCLOPENTENE DERIVATIVE VIA CYCLOADDITION OF METHYL(PHENYL(OR TERT-BUTYL)THIOMETHYL)KETENE

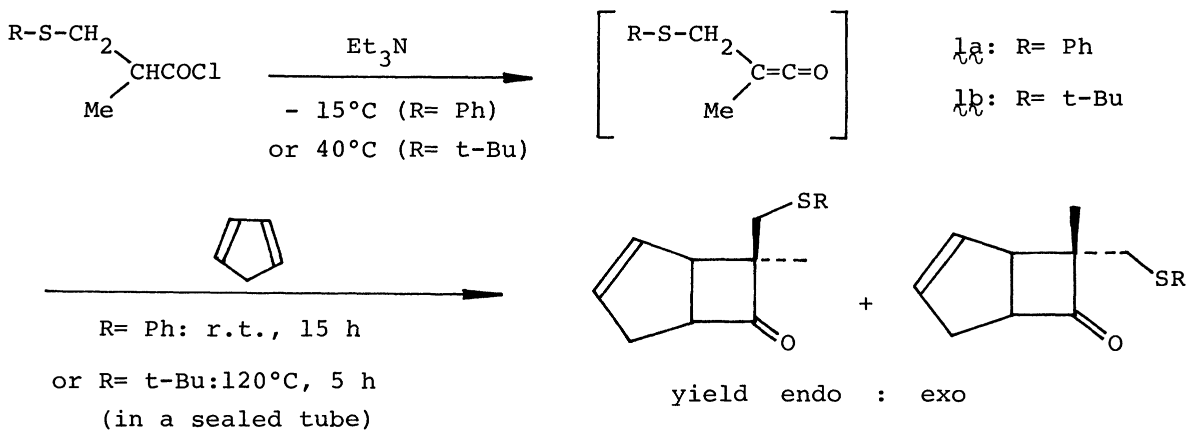
Yoshiki OHSHIRO,* Masaru ISHIDA, Jun-ichi SHIBATA, Toru MINAMI, and Toshio AGAWA
Department of Petroleum Chemistry, Faculty of Engineering, Osaka University
Yamada-oka 2-1, Suita, Osaka 565

Cycloaddition of methyl(phenyl(or tert-butyl)thiomethyl)ketene to cyclopentadiene gave a bicyclic cyclobutanone derivative which was further transformed to cyclopentene systems having alkenyl and carbonyl substituents at vicinal positions.

Ketenes having hetero atoms at the terminal carbon have been interested in the field of organic synthesis because of regioselective ring opening reactions of the cycloadducts, and we reported previously the characteristic transformations of the cyclobutanones derived from methyl(phenylthio)ketene.[1]

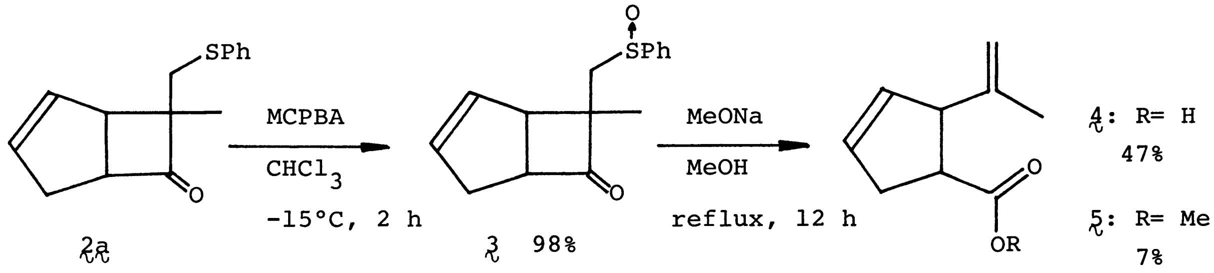
In this paper, we wish to clarify new synthetic routes of cyclopentene systems having alkenyl and carbonyl substituents at vicinal positions via cycloaddition of a new ketene, methyl(phenyl(or tert-butyl)thiomethyl)ketene (1).

The ketene 1 was generated in situ[2] by dehydrochlorination of the corresponding acid chloride[3] with triethylamine in hexane. The ketene 1 reacted with cyclopenta-diene to give the cyclobutanone 2 as a mixture of endo and exo isomers.[4]

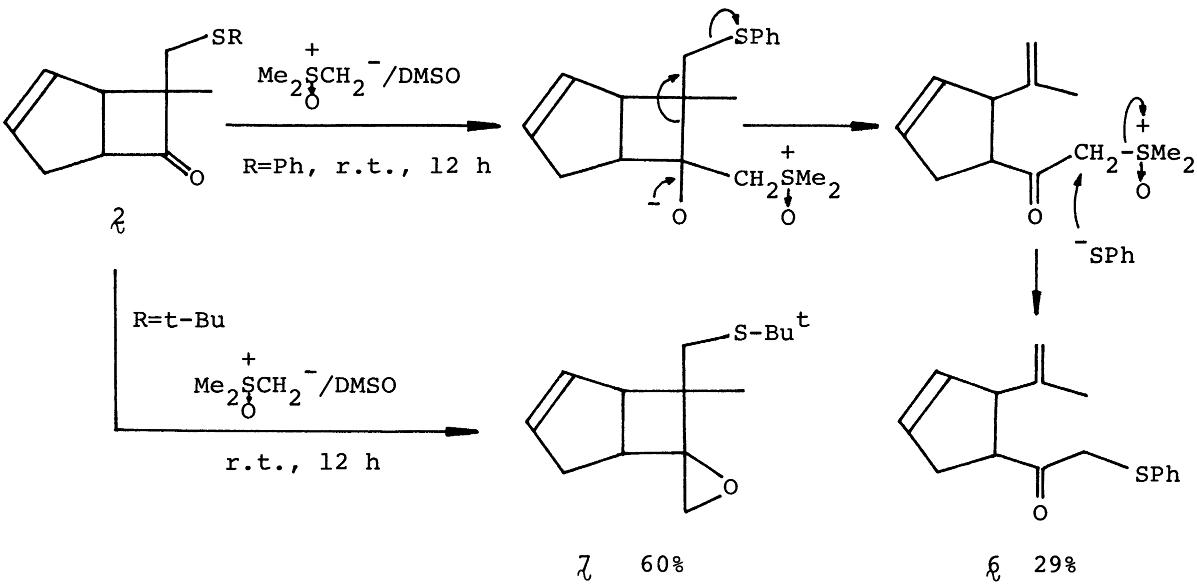


	yield	endo : exo
2a	84%	2 : 1
2b	79%	2 : 1

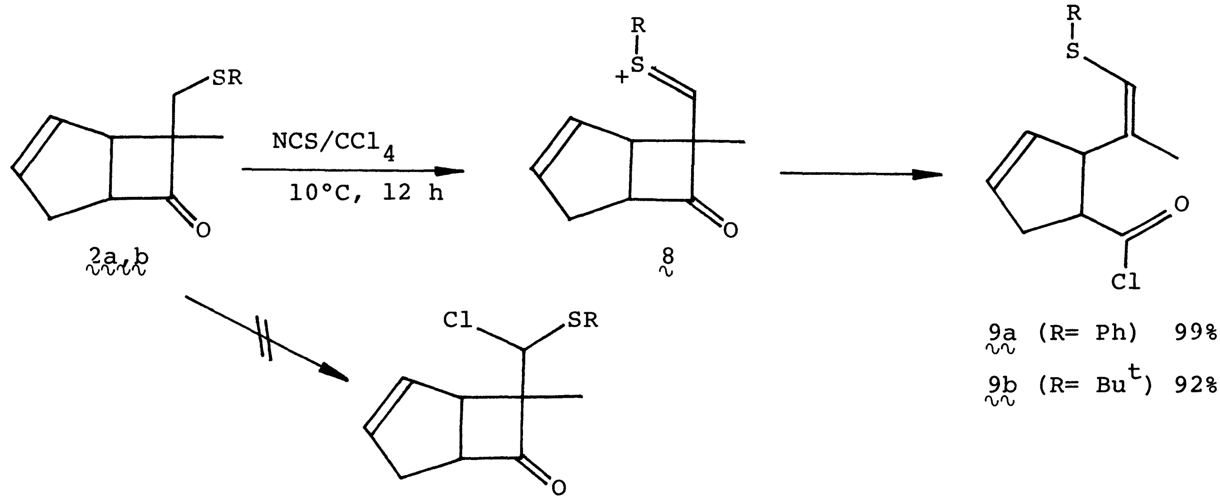
Since it was difficult to isolate each isomer, the following reactions were carried out without separation. After oxidation of the cyclobutanone 2a (R=Ph) by m-chloroperbenzoic acid at -15°C in $CHCl_3$, the resulting sulfoxide 3 was further led to 2-isopropenyl-3-cyclopentenecarboxylic acid (4) and its methyl ester 5 in 47 and 7% yields, respectively, by treatment with sodium methoxide. No transformation was observed for the cyclobutanone 2a under the same conditions.



In the reaction of the cyclobutanone 2a with dimethyloxosulfonium methylide at room temperature, ring cleavage accompanied with migration of the phenylthio group was observed, and 3-isopropenyl-4-phenylthioacetylcyclopentene (6) was obtained in 29% yield.[5] On the other hand, the same reaction with the cyclobutanone 2b (R= t-Bu) gave the epoxide 7 in 60% yield.[6]



Treatment of the cyclobutanone 2a with N-chlorosuccinimide in CCl_4 at 10°C resulted in the exclusive formation of 2-(1-methyl-2-phenylthiovinyl)-3-cyclopentenecarboxyl chloride (9a)[7] in 99% yield without formation of the α-chlorosulfide.[8] The cyclobutanone 2b also gave the acid chloride 9b in 92% yield under the same conditions. The reaction seems to proceed via the intermediate 8.[9] Nucleophilic attack of the chloride ion to the carbonyl carbon of the intermediate 8 causes bond cleavage leading to the formation of the vinyl sulfide group. The Z-configuration of the vinylsulfenyl substituent of the acid chloride 9 was confirmed by ^{13}C-NMR after esterification.[10]



This study shows that transformation of the bicyclic cyclobutanone derived from methyl(phenyl(or tert-butyl)thiomethyl)ketene and cyclopentadiene provides a new method of obtaining cyclopentene systems having alkenyl and carbonyl groups as vicinal substituents. Stereochemical studies of the vicinally substituted cyclopentene derivatives are now in progress.

Acknowledgment: This work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education.

References

1) M. Ishida, T. Minami, and T. Agawa, J. Org. Chem., 44, 2067 (1979).

2) The infrared spectrum of the ketene 1 in ether showed the characteristic absorption of C=C=O at 2100 cm^{-1}.

3) 2-Methyl-3-phenylthiopropionyl chloride was prepared by treatment of thionyl chloride from 2-methyl-3-phenylthiopropionic acid, which was obtained by the reaction of thiophenol and methyl methacrylate in the presence of a catalytic amount of potassium tert-butoxide followed by hydrolysis. Overall yield 78%:

bp 105-109°C/1 Torr. In a similar way, 2-methyl-3-tert-butylthiopropionyl chloride was prepared. Overall yield 64%, bp 58-60°C/1 Torr.

4) The product was isolated by distillation under reduced pressure as a mixture of endo and exo isomers, bp 141-143°C/1.5 Torr. The ratios of endo and exo isomers were determined on the basis of ^{1}H-NMR. **2a**: ^{1}H-NMR ($CDCl_3$) δ 1.10 (s, 3/3H, Me of exo-**2a**), 1.47 (s, 6/3H, Me of endo-**2a**), 2.3-2.7 (m, 2H, CH_2), 3.0-3.7 (m, 1H, CH), 3.07 (s, 4/3H, CH_2S of endo-**2a**), 3.25 (s, 2/3H, CH_2S of exo-**2a**), 3.98 (m, 1H, CH), 5.7-6.0 (m, 2H, CH=CH), 7.1-7.5 (m, 5H, Ph). **2b**: ^{1}H-NMR ($CDCl_3$) δ 1.06 (s, 3/3H, Me of exo-**2b**), 1.30 (s, 18/3H, Bu^t of endo-**2b**), 1.33 (s, 9/3H, Bu^t of exo-**2b**), 1.41 (s, 6/3H, Me of endo-**2b**), 2.3-2.9 (m, 4H, $2CH_2$), 3.0-3.7 (m, 1H, CH), 3.98 (m, 1H, CH), 5.6-6.1 (m, 2H, CH=CH).

5) The infrared spectrum of **6** showed the characteristic absorptions of C=O and $C=CH_2$ at 1705, 1640, and 890 cm^{-1}.

6) Thr infrared spectrum of **7** showed no absorption band of C=O and $C=CH_2$, and its mass spectrum showed the parent peak at m/e 238. The presence of a oxirane ring was confirmed by the characteristic absorption of CH_2 group of the ring at 3060 cm^{-1} in the infrared spectrum and the chemical evidence that the epoxide was transformed into the carbonyl compound thermally.

7) The ^{13}C-NMR spectrum of **9a** showed the signal of the carbonyl carbon at 174.1 ppm in $CDCl_3$.

8) P. Bakuzis and M. L. F. Bakuzis, J. Org. Chem., 42, 2362 (1977).

9) D. L. Tuleen and T. B. Stephens, J. Org. Chem., 34, 31 (1969).

10) Carbonyl carbon: 175.4 ppm; methyl carbon 16.0 ppm; coupling constant between methyl carbon and olefin proton: 4 Hz; C. A. Kingsbury, D. Draney, A. Sopchick, W. Rissler, and D. Durham, J. Org. Chem., 41, 3863 (1976).

(Received December 3, 1981)