Tetrahedron Letters,Vol.26,No.45,pp 5571-5574,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

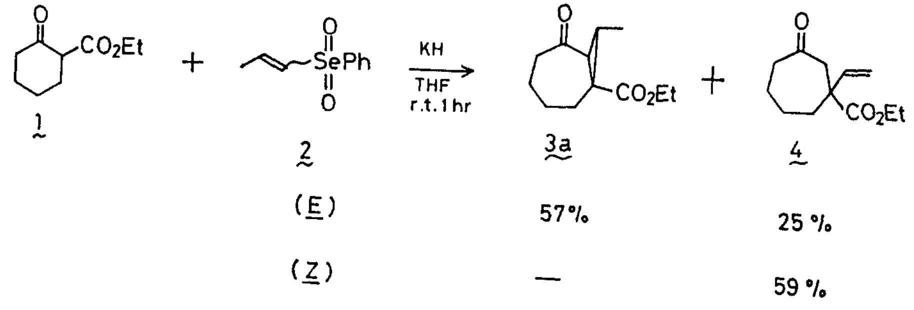
A One-Carbon Ring Enlarged Cyclopropanation or Vinylation Reaction of Cyclic Keto Esters or Sulfones

Tomoo Sugawara and Isao Kuwajima*
Department of Chemistry, Tokyo Institute of Technology, Meguro,
Tokyo 152, Japan

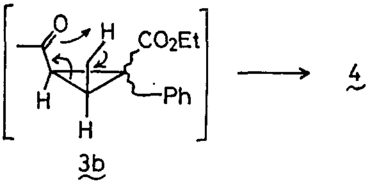
Summary: On treating potassium salts of n-membered cyclic keto esters or sulfones with phenyl 1-propenyl selenone, a one-carbon ring expansion reaction involving cyclopropanation or vinylation takes place to give the corresponding bicyclo[(n - 1).1.0]alkanones or (n + 1)-membered cyclic ketones bearing vinyl group at their 3-position.

In addition to strong electron-attracting behaviors, a much polar linkage between carbon and selenium atoms has provided rather unique character to vinyl selenoxides and vinyl selenones as synthetically useful reagents.[1,2,3] On the basis of such aspects, these selenium-containing functional groups usually activate C=C bonds for conjugate addition of several nucleophiles and further act themselves as excellent leaving groups. These features have allowed an efficient cyclopropanation on their C=C bonds by treating with dibasic nucleophiles such as enolates.[2,3] In the present paper we describe the reaction of vinyl selenones with anionic 2-alkoxycarbonyl- or 2-benzenesulfonylcycloalkanones, which has provided an unprecedented methodology for one-carbon ring enlargement involving cyclopropanation or vinylation. Thus, treatment of potassium salt of ethyl 2-cyclohexanonecarboxylate **1** with phenyl (E)-propenyl selenone **2**-(E)[4] in THF at room temperature led to a predominant formation of the corresponding bicyclo[5.1.0]octane **3a** of ($1R^*,7S^*,8R^*$)-configuration[5] together with a small amount of 1-vinyl-3-cycloheptanone-1-carboxylate **4**, whereas the latter **4** was obtained as a sole product from the reaction with (Z)-propenyl selenone **2**-(Z) under similar conditions (Eq 1). Interestingly, a product **3b** bearing cis-conformation between a methyl group and a ketone function on the cyclopropane has never been detected in both reaction mixtures.

Absence of **3b** apparently indicates that such a product of cis-conformation may be initially formed, but readily undergoes ring opening under present reaction conditions through a proton transfer from methyl to the closely located ketone oxygen to yield the corresponding **4** as shown in Scheme 1.

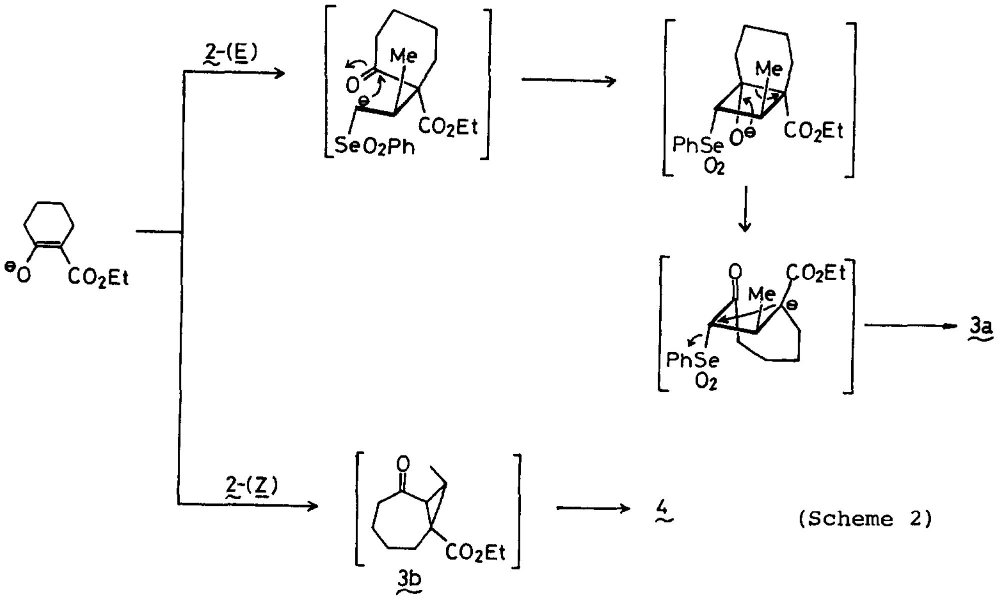


(Eq 1)



(Scheme 1)

The stereochemical results of the reaction course may be rationalized by assuming that, in the reaction with anionic species of rigid conformation,[6]

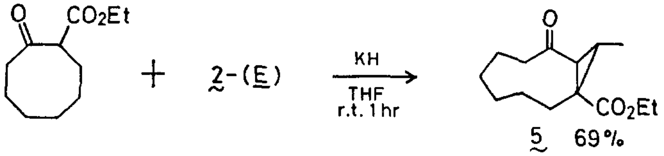


(Scheme 2)

both an initial conjugate addition and a second 1,2-addition[3] take place on the same face of the vinyl selenone predominantly or exclusively. Consequently, the **2**-(E) affords **3a** as shown in Scheme 2, while the **2**-(Z) may initially yield the corresponding bicyclic compound **3b** of $(1R^*,7S^*,8S^*)$ configuration which undergoes ring cleavage to give **4**.

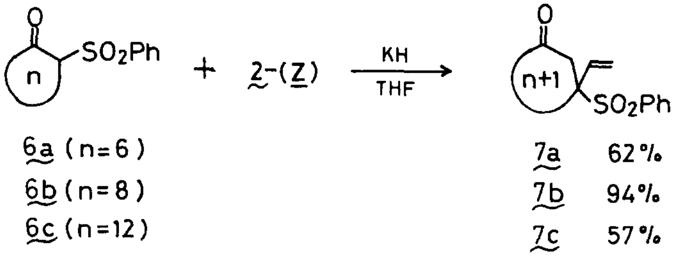
The observed stereocontrol on cyclopropane ring of **3a** as well as selective ring cleavage of **3b** depending on the geometry of **2** used seem to be quite useful for several synthetic purposes.

Similarly, cyclooctanonecarboxylate could be converted to the corresponding 9-membered keto ester **5** exclusively on treating with **2-(E)** (Eq 2).



(Eq 2)

In the reaction with **2**-(Z), cyclic keto sulfones **6a-c** also behave similarly to give the ring-enlarged 3-phenylsulfonyl-3-vinyl cyclic ketones **7a-c**. However, their reactions with **2**-(E) failed to give the cyclopropanation products selectively. For example, treatment of 2-phenylsulfonylcyclohexanone **6a** with **2**-(E) resulted in the complex mixture, from which the same ring opening product **7a** was isolated in 29% yield along with a small amount of the cyclopropyl ketone (14%).



(Eq 3)

In contrast to cyclic keto esters, sulfones react with **2** much more slowly and a higher reaction temperature is usually required for complete consumption of the starting material **2**. During such slow conversion, stereochemical outcome may be disturbed possibly during the process of four-membered ring formation which results in the preferable formation of relatively stable conformation to lead to **7**. As a typical example, the reaction of 2-benzenesulfonylcyclododecanone affords 3-phenylsulfonyl-3-vinylcyclotridecanone **7c** as a sole product irrespective of the geometry of **2**.

Thus, in addition to direct cyclopropanation with dibasic enolates, use of vinyl selenones as conjugate addition acceptors has broaden their synthetic utilities in such aspects as a one-carbon enlarged cyclopropanation including a selective transfer of an acyl group, and selective ring opening of the resulting cyclopropyl ketones, depending on their geometry and the substrates used as nucleophiles.

Acknowledgment This work is partially supported by a Grant from Ministry of Education, Science, and Culture of the Japanese Government.

References

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3) R. Ando, T. Sugawara, and I. Kuwajima, J. Chem. Soc., Chem. Commun., 1514 (1983).
4) By oxidation of the corresponding selenides with m-CPBA, these compounds are obtained as stable colorless crystals. 2-(E): mp 90-92° C. 2-(Z): mp 55-57° C.
5) This conclusion has been deduced from a coupling constant of a hydrogen on the cyclopropane ring of **3a** (CCl_4) appeared at δ 2.44 (d, J = 5.8 Hz, 1H).
6) On geometric conformation of alkali metal enolates: L. M. Jackman and B. C. Lange, Tetrahedron, **33**, 2737 (1977).

(Received in Japan 3 September 1985)