CHEMISTRY LETTERS, pp. 1527-1530, 1987. © 1987 The Chemical Society of Japan

Ring Expansion through [2+2] Photocycloaddition—β-Scission Sequence. Two Carbon Ring Expansions of β-Indanone and β-Tetralone[1]

Hiroshi SUGINOME,* Masahito ITOH, and Kazuhiro KOBAYASHI
Organic Synthesis Division, Department of Chemical Process Engineering,
Faculty of Engineering, Hokkaido University, Sapporo 060

We describe a new method for two carbon ring expansions of 5- and 6-membered rings of β-indanone and β-tetralone through the [2+2] photocycloaddition of the enol ethers of the cyclic ketones followed by the radical cleavage of the fused bond of the cyclobutanols derived from the adducts.

As part of our continuing study to explore the potential of the β-scission reaction of the alkoxyl radicals for organic synthesis, we have recently reported the new synthesis of benzohomotropones through the β-scission of the alkoxyl radicals generated from the cyclobutanols that can be obtained by the [2+2] photocycloaddition of α- and β-naphthol trimethylsilyl ethers with acrylonitrile or methyl acrylate.[2,3]

In this communication we wish to report new synthetically useful ring expansions of β-indanone and β-tetralone as the models of cycloalkanones to functionalized benzocyclooctenone and benzocycloheptenones by the [2+2] photocycloaddition—β-scission sequence.

First, the ring expansion of β-tetralone was studied. The triplet sensitized photocycloaddition of β-tetralone trimethylsilyl enol ether (1)[3] (1 g, 4.6 mmol) to an excess of acrylonitrile (3.2 g, 60.8 mmol) in benzene (35 ml) containing 0.37 mmol of Michler's ketone with a Pyrex-filtered light generated by a 500-W high pressure Hg arc lamp gave a mixture of the *exo*- and *endo*-[2+2] photoadducts 2 and 3 with an expected regioselectivity; these arose from the closure of the most stabilized 1,4-biradical. The isomers were separable on a silica gel column. The removal of the protecting group from 2 and 3 with aq. HCl in THF gave *exo*-3-cyanotricyclo[6.4.0.0^{2,5}]dodeca-1(12),6,8,10-trien-5-ol (4) (mp 109-110 °C) and its *endo*-isomer (5) (bp 150 °C, 0.1 mmHg) (32 and 27%).[4] The assigned stereochemistry of 4 and 5 was established by means of ^{1}H NMR spectroscopy.

Irradiation of *exo*-cyclobutanol 4 (120 mg, 0.6 mmol) in benzene (45 ml) containing HgO (420 mg, 1.8 mmol) and I_2 (491 mg, 1.8 mmol) through a Pyrex filter with a 100-W high pressure Hg arc for 1.5 h gave *cis*-9-cyano-10-iodo-t,r,9,10-tetrahydro-7(8*H*)-benzocyclooctenone (6) (43%); this arose from a regioselective β-scission of the fused bond of the corresponding alkoxyl radical.

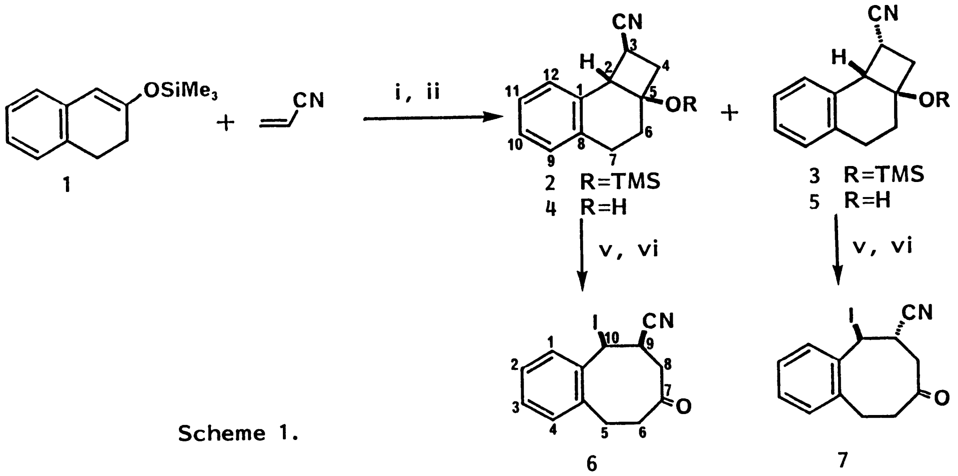
The similar photolysis of *endo* cyclobutanol 5 gave crystalline *trans*-9-cyano-10-iodo-5,6,9,10-tetrahydro-7-(8*H*)-benzocyclooctenone (7) (mp 130-132 °C) (74%). The assigned relative geometry of the iodine and the cyano groups were established by ^{1}H NMR spectroscopy.

Irradiation of (1) (1.0 g, 4.59 mmol) and methyl acrylate (5.0 g, 58 mmol) in benzene (35 ml) containing Michler's ketone (150 mg, 0.56 mmol) under these conditions again took place with the expected regioselectivity and gave a mixture of the *exo*- and *endo*-[2+2] photoadducts (8); these were transformed into an inseparable 6:4 mixture of *exo*- and *endo*-cyclobutanols (9) by treatment with aq. HCl in THF (71% from 1). Irradiation of 9 in benzene in the presence of HgO-I$_2$ under similar conditions as those applied to the β-scission of cyclobutanols 4 and 5 gave a crystalline *exo*-3-methoxycarbonyltricyclo-[6.4.0.0^{2,4}]dodeca-1(12),6,8,10-trien-5-one (10) (mp 103-104 °C) and γ-lactone 11 (35 and 14%). On the other hand, reduction of 9 in diethyl ether with LiALH$_4$ at 0 °C for 30 min gave an inseparable mixture of *exo*- and *endo*-diols 12. The selective acetylation of the diols 12 in diethyl ether with acetyl chloride and triethylamine gave a mixture of monoacetates 13 of the *exo*- and *endo*-diols. The photolysis of *exo*- and *endo*-diols 13 under the same conditions as those applied to the reaction of cyclobutanol 4 gave *cis* and *trans*-9-acetoxymethyl-10-iodo-5,6,9,10-tetrahydro-7(8H)-benzocyclooctenones 14 arose from the regioselective β-scission and a crystalline γ-lactone 15 (mp 133-134 °C) (13% and 46%).

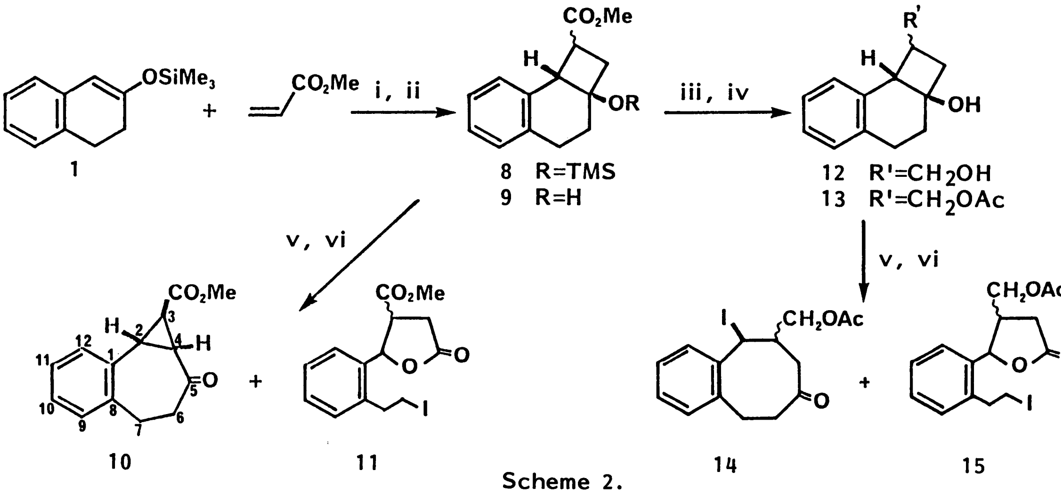
The similar ring expansion of β-indanone was then carried out. Irradiation of β-indanone trimethylsilyl enol ether (16)[3] and acrylonitrile in benzene containing Michler's ketone under the same conditions as those applied to the [2+2] photocycloaddition of trimethylsilyl ether of β-tetralone (1) gave a crystalline *exo*-3-cyanotricyclo-[5.4.0.0^{2,5}undeca-1 (12),7,9,11-trien-5-ol (17) (mp 109-109.5 °C) and its *endo*-isomer (18), separable by means of preparative TLC (27 and 51%). These cycloadducts are those expected for the formation of adducts upon the closure of the most stabilized 1,4-biradical with a regiochemistry that parallels the reported triplet-sensitized cycloaddition of indene and acrylonitrile.[5] Either *exo*-cyclobutanol 17 or *endo*-isomer 18 was then subjected to regioselective fragmentation under the conditions mentioned above to yield crystalline 8-cyano-5,7-dihydro-6*H*-benzocyclohepten-6-one (19) (mp 91-93 °C) (28 and 20%).

Finally, the [2+2] photocycloaddition of enol ether 16[3] and methyl acrylate in benzene containing Michler's ketone under the conditions already mentioned took place in a regioselective manner and gave a mixture of *exo*- and *endo*-photoadducts 20 that arose from the closure of the most stabilized 1,4-biradical. Reduction of the photoadducts 20 with LiALH$_4$ gave a 6:4 mixture of *exo*- and *endo*-diols 21 (53%). The monoacetylation of the mixture of the diols 21 gave a mixture of *exo*- and *endo*-3-acetoxymethyltricyclo[5.4.0.0^{2,5}]undeca-1(12),7,9,11-trien-5-ols (22) (55%). The cyclobutanols 22 were subjected to regioselective fragmentaion under the same conditions as those applied to cyclobutanols 4 and 5. The products in this case, however, were a γ-lactone 23 and a stereoisomeric mixture of δ-lactone 24 (38 and 16%). The structures of 23 and 24 as depicted in Scheme 4 were deduced by means of mass, ^{1}H NMR,and IR spectra.

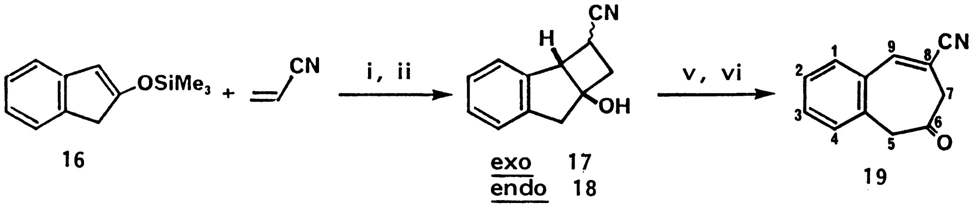
The geneses of the formation of the foregoing three types of product (e.g., 14, 15, and 24) is summarized in Scheme 5. Of these products, the γ- and δ-lactones such as 15 and 24 are formed through the intramolecular combination of the carbonyl



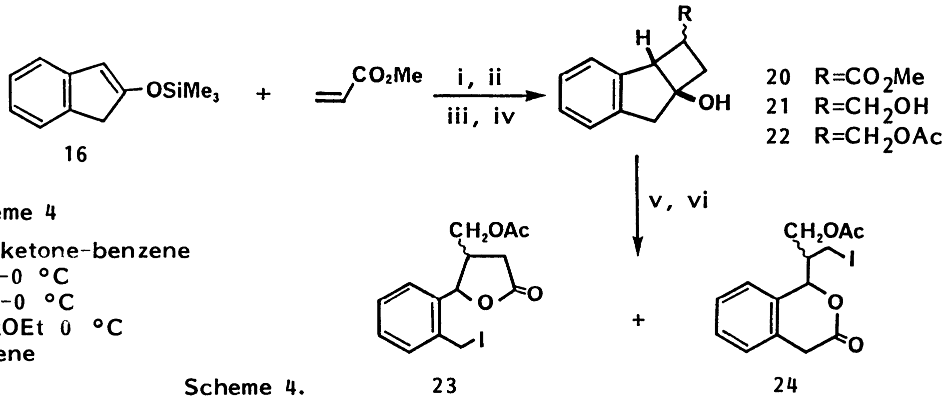
Scheme 1.



Scheme 2.



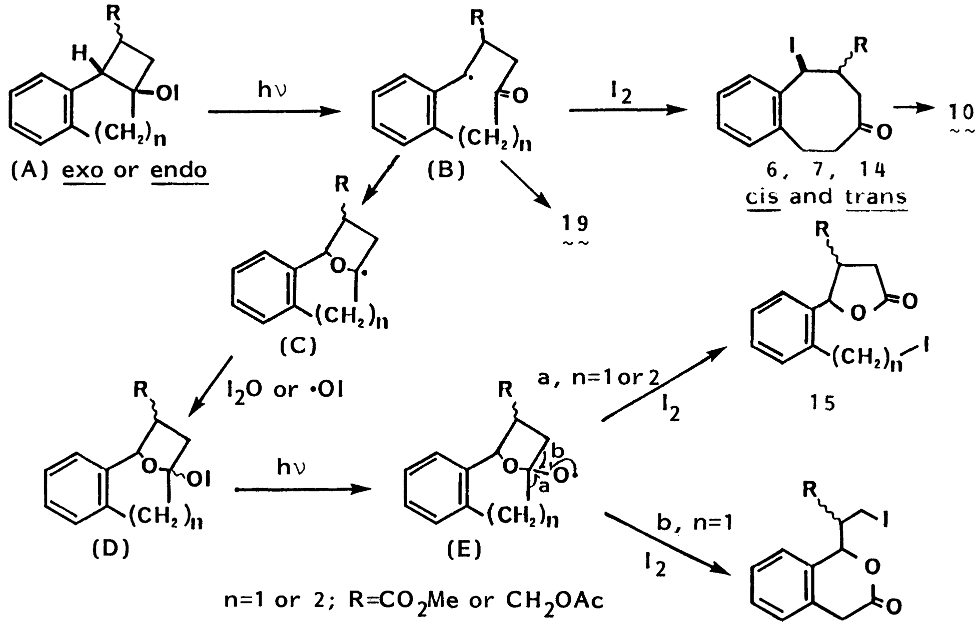
Scheme 3.



Scheme 1 to Scheme 4

i) hν-Michler's ketone-benzene
ii) aq. HCl-THF-0 °C
iii) EtOEt-LiAlH$_4$-0 °C
iv) AcCl-Et$_3$N-EtOEt 0 °C
v) HgO-I$_2$-benzene
vi) hν

Scheme 4.



n=1 or 2; R=CO$_2$Me or CH$_2$OAc

Scheme 5.

oxygen with the benzyl radical to yield a tetrahydrofuranyl radical (C), followed by the β-scission of either the C-C bond a or b of the alkoxyl radicals (E) generated from the second hypoiodite (D). These pathways are parallel to those recently shown by us$^{6)}$ for the formation of the iodo formates in the photolysis of steroidal alcohol hypoiodites.

The further scope of the present method such as its application for the formation of larger rings is being investigated.

We gratefully acknowledge the financial support of the Japanese Ministry of Education and the Takeda Science Foundation.

References

1) Photoinduced Molecular Transformation. Part 93. Part 92. H. Suginome and S. Yamada, Tetrahedron Lett., in press.
2) H. Suginome, C. F. Ryu, and M. Tokuda, J. Chem. Soc., Chem. Commun., 1984, 334; H. Suginome, C. F. Ryu, M. Tokuda, and A. Furusaki, J. Chem. Soc., Perkin Trans. 1, 1985, 327.
3) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, J. Org. Chem., 34, 2324 (1969).
4) Satisfactory analytical and spectral results were obtained for all the new compounds reported in this communication.
5) J. J. McCullough and C. W. Huang, Can. J. Chem., 47, 757 (1969); R. M. Bowman, J. J. McCullough, and J. S. Swenton, ibid., 47, 4503 (1969).
6) H. Suginome and S. Yamada, J. Org. Chem., 49, 3753 (1984).

(Received May 11, 1987)