

Ring Expansion through [2+2] Photocycloaddition— $\beta$ -Scission Sequence.  
Two Carbon Ring Expansions of  $\beta$ -Indanone and  $\beta$ -Tetralone<sup>1)</sup>

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We describe a new method for two carbon ring expansions of 5- and 6-membered rings of  $\beta$ -indanone and  $\beta$ -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  $\beta$ -scission reaction of the alkoxyl radicals for organic synthesis, we have recently reported the new synthesis of benzohomotropones through the  $\beta$ -scission of the alkoxyl radicals generated from the cyclobutanols that can be obtained by the [2+2] photocycloaddition of  $\alpha$ - and  $\beta$ -naphthol trimethylsilyl ethers with acrylonitrile or methyl acrylate.<sup>2,3)</sup>

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

First, the ring expansion of  $\beta$ -tetralone was studied. The triplet sensitized photocycloaddition of  $\beta$ -tetralone trimethylsilyl enol ether (**1**)<sup>3)</sup> (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<sup>2,5</sup>]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%**).<sup>4)</sup> The assigned stereochemistry of **4** and **5** was established by means of <sup>1</sup>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<sub>2</sub> (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(8H)-benzocyclooctenone (**6**) (**43%**); this arose from a regioselective  $\beta$ -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-(8H)-benzocyclooctenone (**7**) (mp 130–132 °C) (**74%**). The assigned relative geometry of the iodine and the cyano groups were established

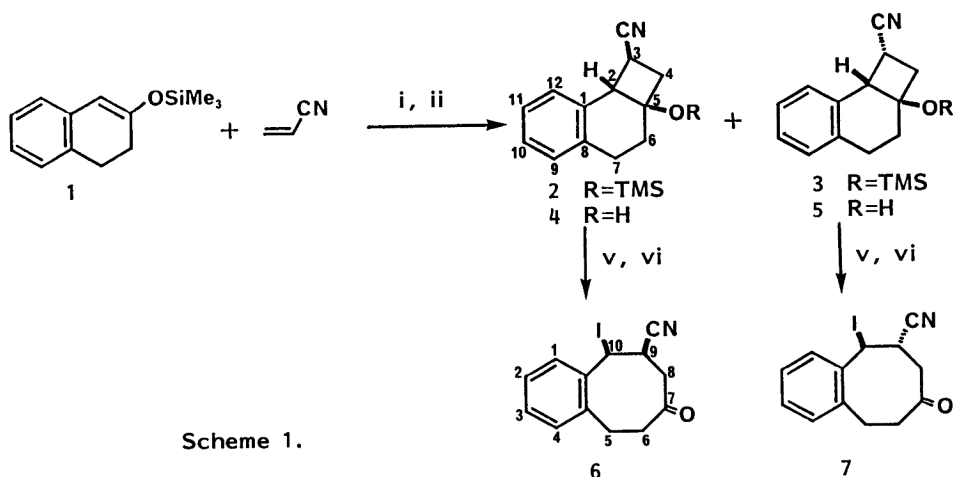
by  $^1\text{H}$  NMR spectroscopy.

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  $\text{HgO-I}_2$  under similar conditions as those applied to the  $\beta$ -scission of cyclobutanols **4** and **5** gave a crystalline exo-3-methoxycarbonyltricyclo-[6.4.0.0<sup>2,4</sup>]dodeca-1(12),6,8,10-trien-5-one (**10**) (mp 103-104 °C) and  $\gamma$ -lactone **11** (35 and 14%). On the other hand, reduction of **9** in diethyl ether with  $\text{LiAlH}_4$  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  $\beta$ -scission and a crystalline  $\gamma$ -lactone **15** (mp 133-134 °C) (13% and 46%).

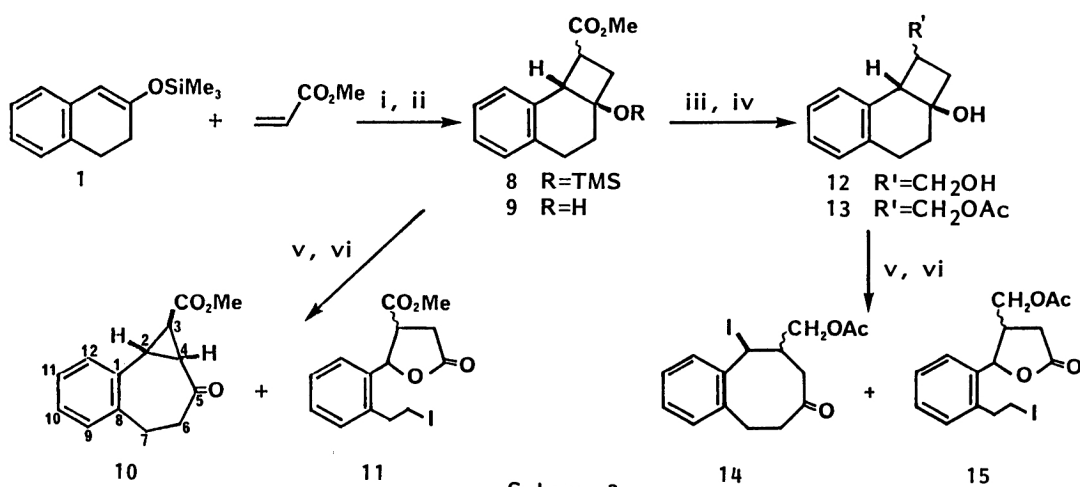
The similar ring expansion of  $\beta$ -indanone was then carried out. Irradiation of  $\beta$ -indanone trimethylsilyl enol ether (**16**)<sup>3)</sup> and acrylonitrile in benzene containing Michler's ketone under the same conditions as those applied to the [2+2] photocycloaddition of trimethylsilyl ether of  $\beta$ -tetralone (**1**) gave a crystalline exo-3-cyanotricyclo-[5.4.0.0<sup>2,5</sup>]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.<sup>5)</sup> 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-6H-benzocyclohepten-6-one (**19**) (mp 91-93 °C) (28 and 20%).

Finally, the [2+2] photocycloaddition of enol ether **16**)<sup>3)</sup> 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  $\text{LiAlH}_4$  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<sup>2,5</sup>]undeca-1(12),7,9,11-trien-5-ols (**22**) (55%). The cyclobutanols **22** were subjected to regioselective fragmentation under the same conditions as those applied to cyclobutanols **4** and **5**. The products in this case, however, were a  $\gamma$ -lactone **23** and a stereoisomeric mixture of  $\delta$ -lactone **24** (38 and 16%). The structures of **23** and **24** as depicted in Scheme 4 were deduced by means of mass,  $^1\text{H}$  NMR, and IR spectra.

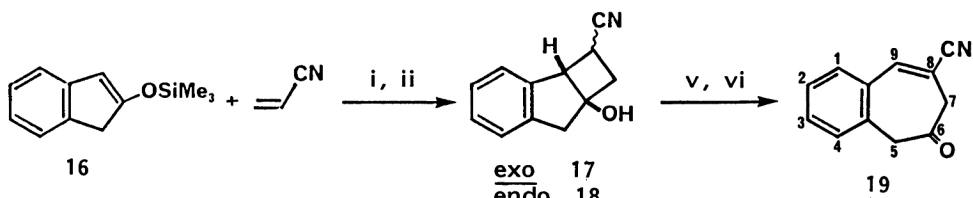
The geneses of the formation of the foregoing three types of product (e.g., **14**, **15**, and **24**) is summarized in Scheme 5. Of these products, the  $\gamma$ - and  $\delta$ -lactones such as **15** and **24** are formed through the intramolecular combination of the carbonyl



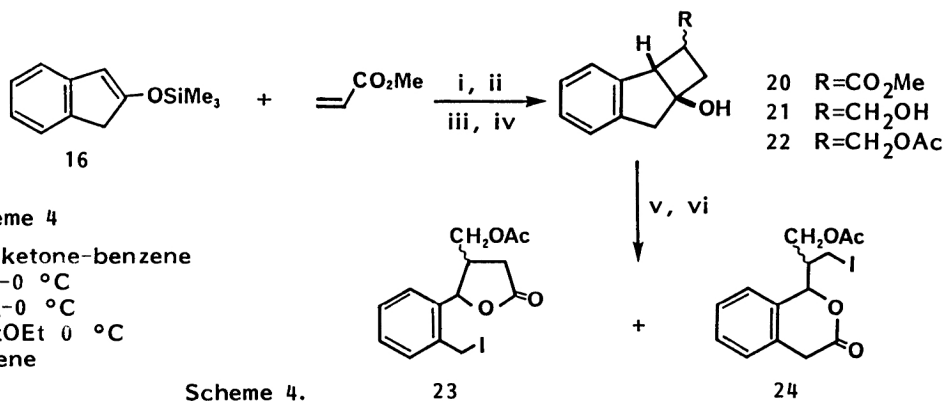
Scheme 1.



Scheme 2.



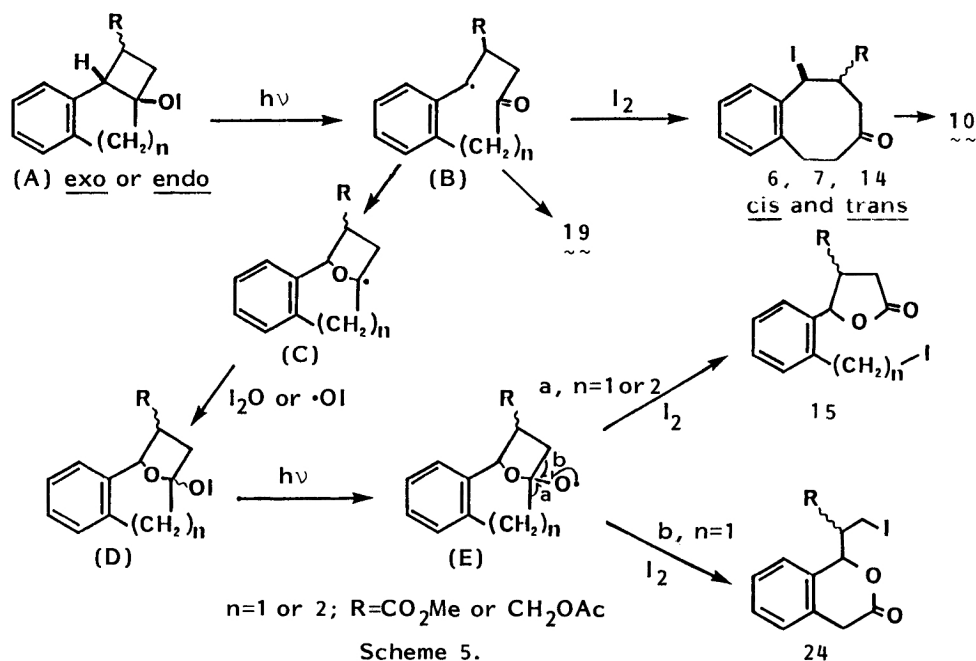
Scheme 3.



Scheme 4.

Scheme 1 to Scheme 4

- i)  $h\nu$ -Michler's ketone-benzene
- ii) aq. HCl-THF-0 °C
- iii) EtOEt-LiAlH<sub>4</sub>-0 °C
- iv) AcCl-Et<sub>3</sub>N-EtOEt 0 °C
- v) HgO-I<sub>2</sub>-benzene
- vi)  $h\nu$



oxygen with the benzyl radical to yield a tetrahydrofuranyl radical (C), followed by the  $\beta$ -scission of either the C-C bond a or b of the alkoxy radicals (E) generated from the second hypoiodite (D). These pathways are parallel to those recently shown by us<sup>6)</sup> 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.

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