

## A Convenient Route to Vicinally Substituted Cyclopentanones via Pinacol Type Rearrangement of Cyclobutanes

Subrata Ghosh\* and Debasis Patra

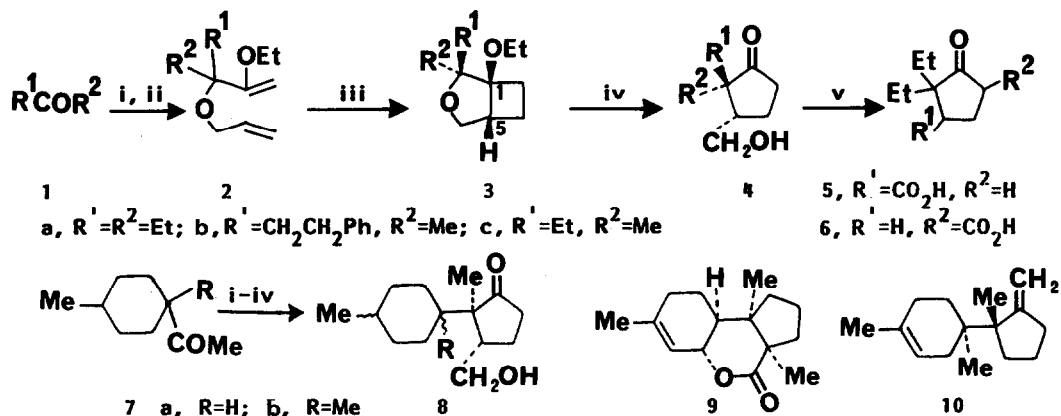
Department of Organic Chemistry, Indian Association for the  
Cultivation of Science, Jadavpur, Calcutta - 700 032, India.

**Abstract :** A convenient route to the vicinally substituted cyclopentanones **4,8** have been developed via rearrangement of oxabicyclo[3.2.0]heptanes obtained through intramolecular [2+2] photocycloaddition in dienes derived from ketones **1, 7**.

Construction of vicinally substituted cyclopentanes is of considerable importance as they are frequently encountered in natural products. They also serve as important rudimentary synthons<sup>1</sup> for the synthesis of complex natural products bearing fused cyclopentanes. Methods of constructing them usually involve conjugate addition-enolate trapping<sup>2</sup> in preformed cyclopentenone derivatives or intramolecular cyclisations.<sup>3</sup> We now report a conceptually different approach for the construction of vicinally substituted cyclopentanones from acyclic ketones. The key step involves pinacol type rearrangement of an alkoxy cyclobutane derivative obtained through intramolecular [2+2] photocycloaddition in an alkene-enol ether derivative derived from a ketone.

In a representative sequence, reaction<sup>4</sup> of diethyl ketone **1a** with ethoxy vinyl lithium followed by alkylation of the carbinol with allyl bromide afforded the diallyl ether derivative **2a**<sup>5</sup> in excellent yield. Irradiation of a diethyl ether solution of **2a** in presence of copper(I) trifluoromethanesulfonate (CuOTf) as catalyst through a quartz immersion well with a Hanovia medium pressure mercury vapour lamp afforded the oxabicyclo[3.2.0]heptane derivative **3a**<sup>6</sup> in 67% yield. Rearrangement of **3a** was accomplished with trifluoromethanesulfonic acid (TFSA) to produce the cyclopentanone **4a** (74%). The structure of the rearrangement product as **4a** arising by migration of the 1,5-bond was established by its oxidation to the acid **5** (69%), m.p. 98°C, which failed to decarboxylate, thus excluding the  $\beta$ -keto acid structure **6** which would arise if rearrangement had involved migration of the 1,7-bond.

The remarkable feature of this approach is the stereoselectivity observed during photocycloaddition and rearrangement when unsymmetrical ketones were employed. Thus, the diallyl ether derivative **2b** gave ca. 5:1 mixture (<sup>1</sup>H NMR) of the photoadducts. The isomer **3b** with the exo bulkier group (CH<sub>2</sub>CH<sub>2</sub>Ph) at C<sub>2</sub> was formed



Reagents : i,  $\text{Bu}^t\text{Li}$ , ethyl vinyl ether, THF,  $-70^\circ\text{C}$  to rt, 50-76%, ii, NaH-THF, allyl bromide, HMPA, reflux, 83-95%, iii,  $h\nu$ ,  $\text{Et}_2\text{O}$ , CuOTf, 60-68%, iv, TFSA,  $\text{CH}_2\text{Cl}_2$ ,  $-78^\circ\text{C}$  to rt, 2h, 25-75%, v,  $\text{CrO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , acetone,  $0^\circ\text{C}$  to rt, 1h.

preferentially as the corresponding copper(I)-diene complex<sup>6b</sup> involved in the cyclisation is less sterically crowded. Rearrangement of this photoadduct mixture afforded a mixture of chromatographically inseparable cyclopentanones in ca. 5:1 ratio. The stereochemical assignment of the major isomer **4b** was made from the shielding of the methyl protons ( $\delta 0.90$ ) relative to the analogous protons in the minor isomer ( $\delta 1.11$ ) in accord with a previous observation.<sup>3b</sup> Similarly, the ketone **1c** gave the cyclopentanone **4c** and its diastereoisomer with ca. 3.8:1 ratio. The generality of this sequence is further demonstrated by transformation of the ketones **7a** and **7b** to the cyclopentanones **8a** and **8b**, the ring systems present in the sesquiterpenes cuprenolide **9**<sup>7</sup> and trichodiene **10**<sup>8</sup> respectively.

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