THERMAL ELECTROCYCLIC REACTION OF 4-CARBOMETHOXY-3-[CIS-2-(2,6,6-TRIMETHYL-1-CYCLOHEXENYL) VINYL] CYCLOHEX-2-EN-1-ONE

Tong Hei KIM and Sachihiko ISOE*

Institute of Organic Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558

Thermal cyclization of titled *cis*-trienone $\underline{3}$ leads to a mixture of tricyclic ketone $\underline{4}$ and an unexpected aromatic ketone $\underline{5}$, the latter being derived by the elimination of methyl group.

In contrast to photochemical reaction of conjugate *cis* hexatriene where the ring opening product is major at the equilibrium state, the thermal reaction gives preferencially cyclized product.¹⁾ The thermal electrocyclic closure of conjugated *cis* hexatriene should be disrotatory with the power of Woodward-Hoffmann rules.

We have already demonstrated the thermal electrocyclic reaction of 7,8-*cis*-10-carbomethoxy- β -ionone enol acetate followed by methanolysis yielding decalone derivative <u>6</u>, which bears exactly adequate functional groups accessible to the synthesis of sesqui and diterpenes.²⁾

In this communication, we describe the first example of thermal electrocyclic reaction involving elimination of methyl group from trienone system $\underline{3}$ where the ε, ζ -double bond is incorporated within a ring.

Starting *cis*-trienone <u>3</u> was prepared as follows. Reaction of β -keto ester <u>1</u> with 1-diethylaminobutan-3-one methiodide (NaH, benzene), and subsequent base treatment (NaOMe) afforded the *trans*-trienone <u>2</u> (40% from <u>1</u>):IR(film) 1735, 1660 cm⁻¹; UV(EtOH) λ_{max} 330 nm; ¹H-NMR(CCl₄) δ 0.98(3H,s), 1.02(3H,s), 1.69(3H,s), 3.66 (3H,s), 5.82(1H,s), 6.03(1H,d,J=16 Hz), 6.53(1H,d,J=16 Hz). Photosensitized isomerization³ of *trans*-trienone <u>2</u> (hv, benzathrone as sensitizer, THF, 2 h) gave the *cis*-trienone <u>3</u> (> 90%):¹H-NMR(CCl₄) δ 5.82(1H,d,J=13 Hz), 5.98(1H,s), 6.2(1H,d J=13 Hz). Thermal cyclization was carried out at various temperature ranges (170-250 °C) and time durations (0.5 to 9 h) yielding compound 5⁴) (25-28% from cis-trienone <u>3</u>). For example, heating <u>3</u> at 220 °C for 30 min afforded a cyclized product $\underline{4}^{4)}$ (18%):IR(film) 1735, 1710, 1310, 1170 cm⁻¹; UV(EtOH) λ_{max} 258 nm; ¹H-NMR(CCl₄) δ 1.09(3H,s), 1.15(6H,s), 2.86(1H,s), 3.66(3H,s), 5.54(1H,d,J=6 Hz), 5.75(1H,d,J=6 Hz), and unexpected aromatized product <u>5</u> (28%):IR(film) 1740, 1680, 1165 cm⁻¹; UV(EtOH) λ_{max} 272 nm; ¹H-NMR(CCl₄) δ 1.27(3H,s), 1.3(3H,s), 3.67(3H,s), 6.93(1H,d,J=8 Hz), 7.33(1H,d,J=8 Hz), and recovered trienone (28%) (*trans*-trienone <u>2</u>: cis-trienone <u>3</u> = 1 : 3). Cyclization product <u>4</u> and <u>5</u> could be useful intermediates for the synthesis of tanshinones and other tricyclic diterpenes.



Scheme 1

References

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- 3) V. R. Y. Butt, C. Yang, P. Yang, and R. S. H. Liu, J. Org. Chem., <u>38</u>, 1247 (1973).
- 4) 4 and 5 gave satisfactory elemental analyses.

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