CHEMISTRY LETTERS, pp. 539-540, 1983.

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

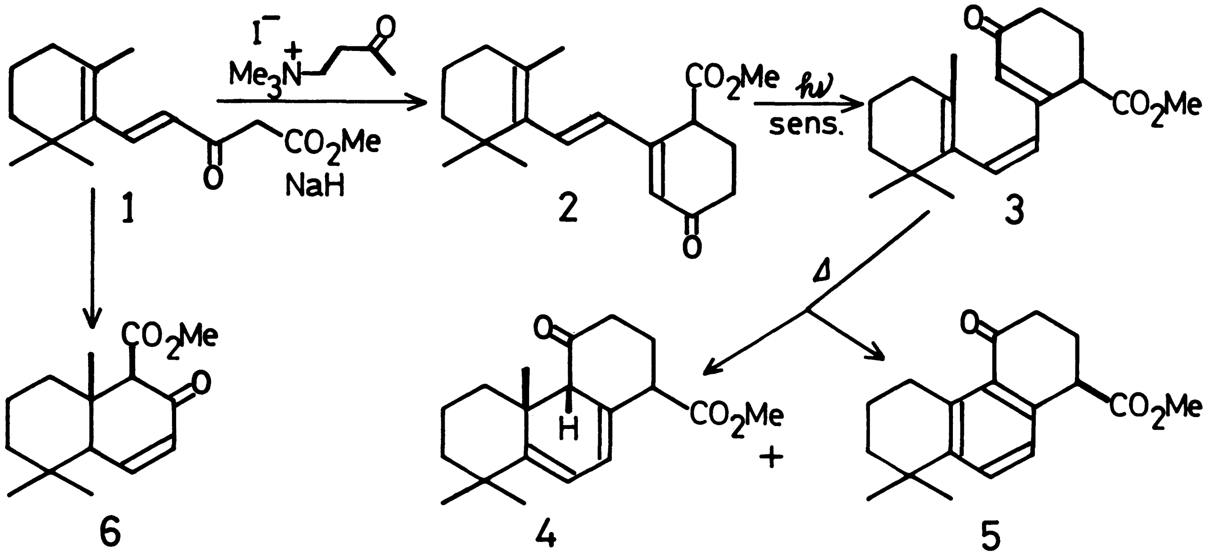
Thermal cyclization of titled *cis*-trienone 3 leads to a mixture of tricyclic ketone 4 and an unexpected aromatic ketone 5, the latter being derived by the elimination of methyl group.

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 6, 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 3 where the ε,ζ-double bond is incorporated within a ring.

Starting *cis*-trienone 3 was prepared as follows. Reaction of β-keto ester 1 with 1-diethylaminobutan-3-one methiodide (NaH, benzene), and subsequent base treatment (NaOMe) afforded the *trans*-trienone 2 (40% from 1):IR(film) 1735, 1660 cm^{-1}; UV(EtOH)λ_{max} 330 nm; ^{1}H-NMR(CCl_4)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 isomerization[3)] of *trans*-trienone 2 (hν, benzathrone as sensitizer, THF, 2 h) gave the *cis*-trienone 3 (> 90%):^{1}H-NMR(CCl_4)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 5[4)] (25-28% from *cis*-trienone 3). For example, heating 3 at 220 °C for 30 min afforded a cyclized product 4[4] (18%):IR(film) 1735, 1710, 1310, 1170 cm^{-1}; UV(EtOH)λ_{max} 258 nm; ^{1}H-NMR(CCl_4)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 5 (28%):IR(film) 1740, 1680, 1165 cm^{-1}; UV(EtOH)λ_{max} 272 nm; ^{1}H-NMR(CCl_4)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 2 : *cis*-trienone 3 = 1 : 3). Cyclization product 4 and 5 could be useful intermediates for the synthesis of tanshinones and other tricyclic diterpenes.



Scheme 1

References

1) K. J. Crowley and S. G. traynor, Tetrahedron Lett., 1975, 3555; G. Frater, Helv. Chim. Acta, 57, 2446 (1974); R. Ramage and A. Sattar, J. Chem. Soc., Chem. Commun., 1970, 173.

2) S. Katsumura and S. Isoe, Chem. Lett., 1982, 1689; A. Kimura, S. Katsumura, and S. Isoe, ibid., 1983, 15.

3) V. R. Y. Butt, C. Yang, P. Yang, and R. S. H. Liu, J. Org. Chem., 38, 1247 (1973).

4) 4 and 5 gave satisfactory elemental analyses.

(Received February 15, 1983)