CHEMISTRY LETTERS, pp. 1421-1424, 1983.

NEW SYNTHESIS OF CYCLOPENTENOL AND SPIRO[4.5]DECANOL DERIVATIVES VIA INTRAMOLECULAR PHOTO-OXETANE FORMATION

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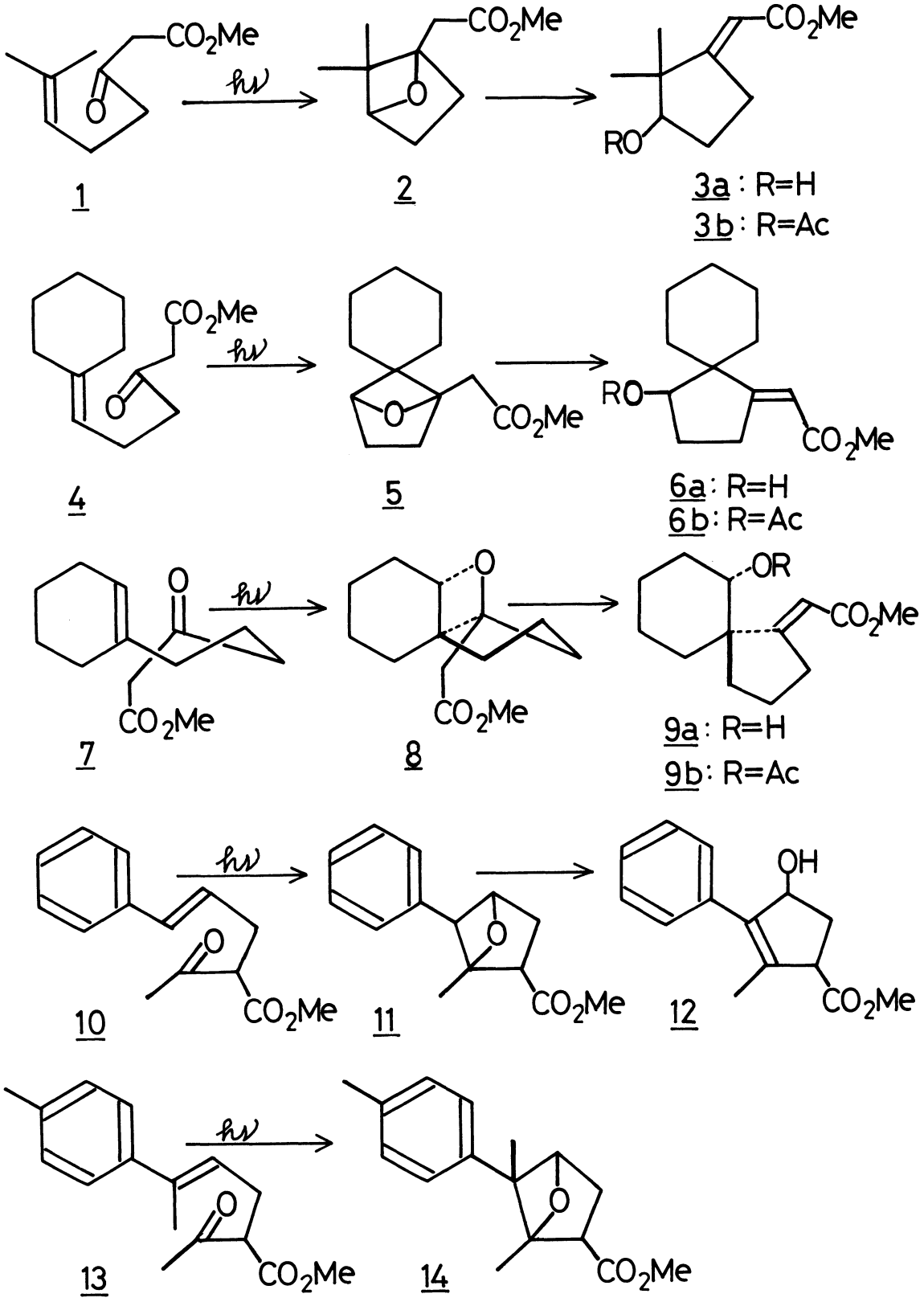
Cyclopentenol and spiro[4.5]decanol derivatives accessible to natural products were synthesized in moderate yield by the irradiation of olefinic β-keto esters followed by treatment with sodium hydride.

Photochemical cycloaddition reactions between olefins and aldehydes or ketones have long been known to result in the formation of oxetanes.[1] Photochemistry of γ,δ-unsaturated ketones as intramolecular examples of this type reaction have also been well studied.[2] In this paper, we describe the first examples of the facile formation of cyclopentenol and spiro[4.5]decanol derivatives from acyclic, exocyclic, endocyclic and aromatic ring conjugated olefinic β-keto esters by irradiation followed by selective cleavage of C-O bond of resulting oxetanes with sodium hydride. General reaction procedure was shown below. An ice-cooled solution of olefinic β-keto ester 1[3] in n-hexane (1.0 g in 1.2 l) was irradiated with a 450W high pressure mercury lamp through Pyrex filter. After 19 hours an oxetane 2[4] (22.6%) and unreacted olefinic β-keto ester 1 (47.7%) was isolated by thin-layer chromatography. Treatment of 2 with sodium hydride (1.3 eq, benzene reflux, 20 min) followed by acetylation gave cyclopentenol derivative 3b[4] (65.5%). Irradiation of olefinic β-keto esters 4 and 7[3] under similar conditions led to the formation of oxetanes 5[4] and 8[4] (conversion yield of 28.7% and 66.4% respectively). 5[3] and 8[3] were converted into spiro[4.5]decanol derivatives 6b[4] and 9b[4] (69.5% and 15%) by above method (i NaH, benzene, ii Ac_2O, pyridine). Next, irradiation of olefinic β-keto ester 10[3] followed by thin-layer chromatography afforded directly cyclopentenol derivative 12[4] (conversion yield 46.5%) via oxetane 11.[4] While, irradiation of olefinic β-keto ester 13[3] followed by thin-layer chromatography led to the isolation

of oxetane 14[4] (conversion yield 46.5%). Cyclopentenol and spiro[4.5]decanol derivatives thus obtained could be useful for the synthesis of laurene and other sesquiterpens.



References

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2) N. C. Yang, M. Nussini, and D. R. Coulson, Tetrahedron Lett., 1965, 1525.

3) Olefinic β-keto esters (1, 4, 7, 10, and 13) were prepared as follows. Treatment of 6-methyl-5-heptene-2-one with dimethyl carbonate (NaH, benzene, reflux) gave olefinic β-keto ester 1. Treatment of cyclohexanone with 4,4-ethylenedioxypentyl triphenyl phosphonium bromide (n-BuLi, THF, 0°C) followed by deprotection and condensation with dimethyl carbonate (NaH, dioxane, reflux) afforded olefinic β-keto ester 4. Treatment of 2-(1-cyclohexen-1-yl)-ethyl bromide with methyl acetoacetate (NaOMe, MeOH, reflux) afforded corresponding β-keto ester, which was converted into olefinic β-keto ester 7, by the following sequence: (1) hydrolysis, (2) decarboxylation, and (3) condensation with dimethyl carbonate(NaH, dioxane, reflux). Cinnamyl bromide and 3-(p-tolyl)-2-butenyl bromide were converted into corresponding olefinic β-keto esters 10 and 13 respectively by treatment with methyl acetoacetate (NaOMe, MeOH, reflux). Satisfactory spectral data (IR, ^{1}H NMR, and UV) for 1, 4, 7, 10, and 13 were obtained.

1: IR(film) 1745, 1717, 1647, and 1625 cm^{-1}; UV(EtOH) 247 nm, UV(EtOH-NaOH) λ_{max} 275 nm; ^{1}H NMR(CCl_4) δ 1.60(6H,s), 3.32(s, keto form) 3.63(3H,s), 4.87(s, enol form), 5.07(1H, t, J=5 Hz).

4: IR(film) 1749, 1719, 1652, and 1625 cm^{-1}; UV(EtOH) λ_{max} 246 nm, UV(EtOH-NaOH) λ_{max} 276 nm; ^{1}H NMR(CCl_4) δ 1.52(6H, br), 3.27(s, keto form), 3.68(3H,s), 4.85 (s, enol form), 4.94(1H, t, J=6 Hz).

7: IR(film) 1745, 1720, and 1625 cm^{-1}; UV(EtOH) λ_{max} 248 nm, UV(EtOH-NaOH) λ_{max} 278 nm; ^{1}H NMR(CCl_4) δ 3.28(s, keto form), 3.68(3H,s), 4.85(s, enol form), 5.32(1H,m).

10: IR(film) 1745, 1721, and 1610 cm^{-1}; UV(EtOH) λ_{max} 249 nm, UV(EtOH-NaOH) λ_{max} 277 nm; ^{1}H NMR(CCl_4) δ 2.16(3H,s), 2.66(2H, t, J=6 Hz), 3.43(1H, t, J=6 Hz), 3.66(3H,s), 5.96(1H,m), 6.48(1H,m), 7.16(5H,m).

13: IR($CHCl_3$) 1740, 1715, 1240, and 1155 cm^{-1}; UV(EtOH) λ_{max} 250 nm; ^{1}H NMR(CCl_4)

δ 2.00(3H,s), 2.14(3H,s), 2.31(3H,s), 2.63(1H, t, J=7 Hz), 3.66(3H,s), 5.48 (1H, t, J=7 Hz), 6.83-7.33(4H,br.s); Mass 260(M^+).

4) Satisfactory spectral data (IR, ^{1}H NMR, and UV) and elemental analyses for 2, 3a, 3b, 5, 6a, 6b, 8, 9b, 12, and 14 were obtained. Stereochemistries of cyclopentenol derivative 12 and oxetane 14 are unknown.

2: IR(CCl_4) 1744, 1202, and 1167 cm^{-1}; ^{1}H NMR(CCl_4) δ 0.77(3H,s), 1.34(3H,s), 2.47(1H, d, J=15 Hz), 2.73(1H, d, J=15 Hz), 3.60[4H(1H: α-proton of ether)]; Mass 184(M^+). 3a: IR(CCl_4) 3400, 1717, and 1654 cm^{-1}; UV(EtOH) λ_{max} 223 nm; ^{1}H NMR(CCl_4) δ 1.06(6H,s), 3.61(3H,s), 3.74(1H, t, J=7 Hz), 5.75(1H, t, J=3 Hz). 3b: IR(CCl_4) 1743, 1721, and 1657 cm^{-1}; UV(EtOH) λ_{max} 221 nm; ^{1}H NMR(CCl_4) δ 1.07(3H,s), 1.10(3H,s), 1.97(3H,s), 3.64(3H,s), 4.85(1H, t, J=5 Hz), 5.60(1H, t, J=3 Hz).

5: IR(CCl_4) 1743, 1450, and 1436 cm^{-1}; Mass 224(M^+). 6a: IR(CCl_4) 3400, 1723, and 1641 cm^{-1}; UV(EtOH) λ_{max} 223 nm; ^{1}H NMR(CCl_4) δ 3.67(3H,s), 4.25(1H,m), 5.67(1H,m).

6b: IR(CCl_4) 1741, 1726, and 1649 cm^{-1}; UV(EtOH) λ_{max} 227 nm; ^{1}H NMR(CCl_4) δ 1.97(3H,s), 3.67(3H,s), 5.37(1H,m), 5.67(1H, t, J=3 Hz).

8: IR(film) 1740, 1210, and 1175 cm^{-1}; ^{1}H NMR(CCl_4) δ 2.73(2H,s), 3.56(3H,s), 4.07(1H, t, J=16 Hz). 9b: IR(CCl_4) 1735, 1718, and 1640 cm^{-1}; ^{1}H NMR(CCl_4) δ 1.96(3H,s), 2.92(2H,m), 3.64(3H,s), 5.34(1H,m), 5.62(1H,m).

12: IR(CCl_4) 3400, 1746 and 1722 cm^{-1}; ^{1}H NMR(CCl_4) δ 1.72(3H,s), 2.68(1H, q, J=4 Hz), 3.66(3H,s), 4.78(1H, t, J=2 Hz), 6.92(2H,m), 7.24(3H,m); Mass 232(M^+).

14: mp 45-47°C, IR(CCl_4) 1740, 1200, and 1170 cm^{-1}; ^{1}H NMR(CCl_4) δ 1.58(6H,s), 2.36(3H,s), 2.82(1H, q, J=9 Hz, J=4 Hz), 3.72(3H,s), 4.50(1H, d, J=1 Hz), 6.86(2H, d, J=8 Hz), 7.18(2H, d, J=8 Hz); Mass 260(M^+).

(Received August 3, 1983)