CHEMISTRY LETTERS, pp.389-392, 1972. Published by the Chemical Society of Japan

PHOTOCHEMISTRY OF FUKINONE AND PULEGONE

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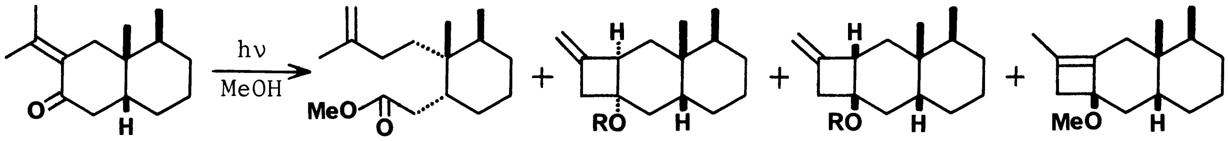
Fukinone (I), a sesquiterpenic ketone containing a conjugated double bond in cisoid form, on photolysis in methanol solution gave methyl ester (III), stereoisomeric cyclobutanols (IVa and Va), and methyl ether (VI). Photolysis of pulegone (II), a monoterpenic analogue of I, afforded quite similar results.

Although photo-induced reactions of cyclohexenone derivatives have been investigated extensively,1) little is known about the photochemistry of the derivatives of a six-membered ring ketone conjugated with an exo-cyclic double bond. The present communication describes the results of UV irradiation of fukinone (I)2) and pulegone (II), terpenic compounds containing cisoid enone systems.

The solution of fukinone (I) in MeOH was irradiated with a 400W high pressure Hg-lamp until the starting material was dissapeared. The reaction mixture was subjected to SiO_2 column chromatography and preparative GLC to give methyl ester (III), stereoisomeric cyclobutanols (IVa and Va), and methyl ether (VI).



I

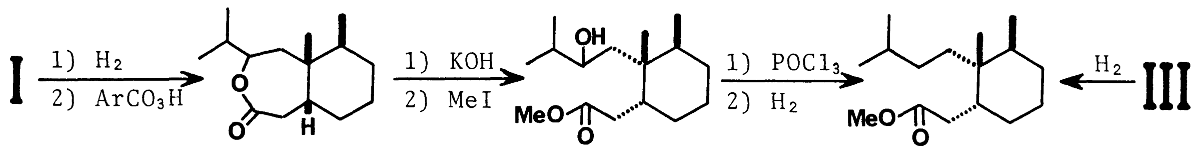
III 10%

IVa R=H 5%
IVb R=Ac

Va R=H 11%
Vb R=Ac

VI 2%

Methyl ester (III), $C_{16}H_{28}O_2$. A colorless oil, $[\alpha]_D^{25}$ +26° (c=1.0 in MeOH). MS: m/e 252 (M^+), 109 (base peak); IR: 3040, 1640, 880 ($H_2C=C$), 1735 cm^{-1} (CO_2Me); NMR: $\delta(CCl_4)$ 0.83 (d, J=6 Hz, Me-CH), 0.87 (s, Me-C), 1.67 (s, Me-C=C), 3.54 (s, MeO), 4.57 (br s, $H_2C=C$). Catalytic hydrogenation of III gave a dihydro derivative, which was identical with the authentic compound, synthesized independently from I as follows;



The cyclobutanols (IVa and Va) were obtained at first as a mixture of the stereoisomers, which upon acetylation gave two acetates (IVb and Vb). Each cyclobutanol was isolated from the acetate mixture by SiO_2 column chromatography followed by alkaline hydrolysis.

Cyclobutanol (IVa), $C_{15}H_{24}O$. A colorless oil, $[\alpha]_D^{25}$ +90° (c=1.0 in MeOH). MS: m/e 220 (M^+), 109 (base peak); IR: 3350 (OH), 3050, 1680, 878 cm^{-1} ($H_2C=C$); NMR: $\delta(CCl_4)$ 0.77 (d, J=6 Hz, Me-CH), 0.90 (s, Me-C), 2.38 (s, OH), 2.65 (m, $H_2C-C=C$ and $HC-C=C$), 4.75 (m, $H_2C=C$).

Cyclobutanol (Va), $C_{15}H_{24}O$. A colorless oil, $[\alpha]_D^{25}$ -27° (c=0.9 in MeOH). MS: m/e 220 (M^+), 109 (base peak); IR: 3350 (OH), 3050, 1680, 878 cm^{-1} ($H_2C=C$); NMR: $\delta(CCl_4)$ 0.75 (d, J=6 Hz, Me-CH), 0.83 (s, Me-C), 1.92 (s, OH), 2.52 (m, $H_2C-C=C$), 2.7 (m, $HC-C=C$), 4.77 (m, $H_2C=C$). The Rf-values (SiO_2-TLC) of the acetates are IVb > Vb.

The structures of IVa and Va including their stereochemistry were established from the NMR study using a chemical shift reagent. On addition of $Eu(DPM)_3$[3] the signals due to the protons in the vicinity of the OH groups showed remarkable downfield shifts clearly indicating the steric nature of these compounds. The movements of the chemical shifts of IVa and Va upon the addition of the reagent are shown in Figure. In the case of IVa the bridge head methine proton (7-H) as well as 9α-H and 12α-H showed large downfield shifts but the shift of 10-H was not

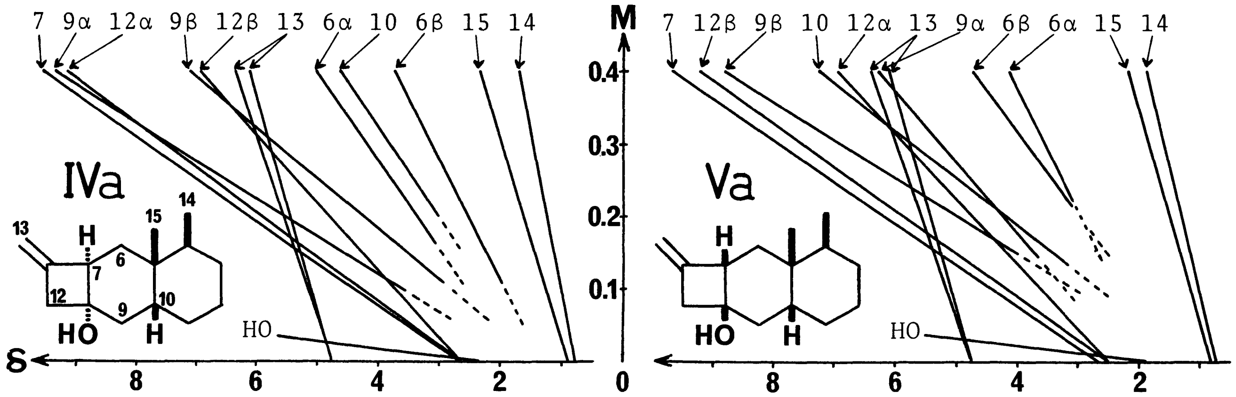
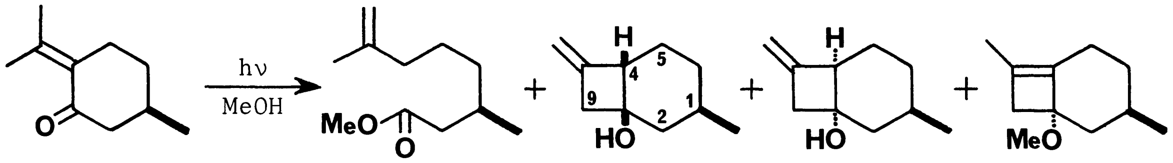


Figure. Dependence of the chemical shifts of IVa and Va upon the concentration of $Eu(DPM)_3$ added. (M = mole of $Eu(DPM)_3$ / mole of IVa or Va) so large, suggesting that the stereochemistry of IVa is cis-anti-cis. On the other hand, both 7-H and 10-H as well as 9β-H and 12β-H of Va showed large downfield shifts upon $Eu(DPM)_3$ addition indicating the cis-syn-cis structure of Va. All these assignments of the proton signals were consistent with the spin-spin decoupling experiments.

Methyl ether (VI), $C_{16}H_{26}O$. A colorless oil. MS: m/e 234 (M^+), 28 (base peak); IR: no OH and C=O bands; NMR: $\delta(CCl_4)$ 0.72 (d, J=6 Hz, Me-CH), 0.90 (s, Me-C), 1.61 (br s, Me-C=C), 3.05 (s, MeO). The structure of VI was confirmed by the NMR spectra taken after the addition of $Eu(DPM)_3$. When the molar ratio of $Eu(DPM)_3$ to VI was 0.7 the δ-values were as follows; 1.55 (d, J=6 Hz, Me-CH), 1.62 (s, Me-C), 2.66 (br s, Me-C=C), 4.04 (d, J=12 Hz, 12α-H), 4.19 (d, J=14 Hz, 6α-H), 5.03 (br d, J=14 Hz, 6β-H), 5.16 (t, J=13 Hz, 9α-H), 5.28 (br d, J=12 Hz, 12β-H), 6.05 (br d, J=13 Hz, 10-H), 8.92 (br d, J=13 Hz, 9β-H), 9.97 (s, MeO).



II VII 2% VIII 11% IX 8% X 1%

Photolysis of d-pulegone (II) was performed similarly as in fukinone (I) and essentially similar results were obtained. The products, isolated and characterized, were methyl ester (VII), cyclobutanols (VIII and IX), and methyl ether (X), which corresponded respectively to III, IVa, Va, and VI, obtained from I. All the spectroscopic data are in good agreement with the proposed structures.

Methyl ester (VII), $C_{11}H_{20}O_2$. A colorless oil, $[\alpha]_D^{25}$ +9° (c=1.0 in MeOH). MS: m/e 184 (M^+), 69 (base peak); IR: 3060, 1650, 890 ($H_2C=C$), 1740 cm^{-1}(CO_2Me); NMR: $\delta(CCl_4)$ 0.91 (d, J=6 Hz, Me-CH), 1.66 (br s, Me-C=C), 3.57 (s, MeO), 4.61 (br s, $H_2C=C$).

Cyclobutanol (VIII), $C_{10}H_{16}O$. Colorless needles, mp 40-40.5°, $[\alpha]_D^{25}$ -66° (c=0.9 in MeOH). MS: m/e 152 (M^+), 151 (M-1), 109 (base peak); IR: 3300 (OH), 3050, 1680, 875 cm^{-1}($H_2C=C$); NMR: $\delta(CCl_4)$ 0.96 (d, J=6 Hz, Me-CH), 2.29 (s, OH), 2.56 (m, $H_2C-C=C$), 2.73 (m, HC-C=C), 4.75 (m, $H_2C=C$); after the addition of $Eu(DPM)_3$ (in the molar ratio of 0.5) 3.43 (d, J=7 Hz, Me-CH), 6.28 and 6.46 (each q, J=1.6 Hz, $H_2C=C$), 7.10 (br d, J=15 Hz, 9α-H), 7.37 (dd, J=14 and 4 Hz, 2α-H), 9.48 (dd, J=14 and 8 Hz, 2β-H), 9.53 (br d, J=15 Hz, 9β-H), 10.05 (m, 4-H).

Cyclobutanol (IX), $C_{10}H_{16}O$. Colorless prisms, mp 55-56°, $[\alpha]_D^{25}$ +58° (c=0.9 in MeOH). MS: m/e 152 (M^+), 151 (M-1), 109 (base peak); IR: 3350 (OH), 3050, 1680, 875 cm^{-1} ($H_2C=C$); NMR: $\delta(CCl_4)$ 0.85 (d, J=5 Hz, Me-CH), 2.48 (m, $H_2C-C=C$), 2.63 (s, OH), 2.75 (m, HC-C=C), 4.74 (m, $H_2C=C$); after the addition of $Eu(DPM)_3$ (in the molar ratio of 0.5) 2.58 (d, J=6 Hz, Me-CH), 5.82 (t, J=13 Hz, 2β-H), 6.35 and 6.49 (each m, $H_2C=C$), 7.31 (d, J=13 Hz, 9β-H), 7.4 (m, 1α-H), 9.77 (br d, J=13 Hz, 9α-H), 9.98 (br d, J=13 Hz, 2α-H), 10.43 (m, 4-H). The Rf-values (SiO_2-TLC) were VIII > IX.

Methyl ether (X), $C_{11}H_{18}O$. A colorless oil. MS: m/e 166 (M^+), 151 (base peak); IR: no OH and C=O bands; NMR: $\delta(CCl_4)$ 0.84 (d, J=6 Hz, Me-CH), 1.62 (br s, Me-C=C), 3.06 (s, MeO); after the addition of $Eu(DPM)_3$ (in the molar ratio of 0.5) 1.12 (d, J=6 Hz, Me-CH), 2.56 (br s, Me-C=C), 3.94 (br d, J=13 Hz, 9β-H), 3.95 (t, J=12.5 Hz, 2β-H), 4.7 (m, 5α-H), 5.11 (br d, J=13 Hz, 9α-H), 5.6 (m, 1α-H), 8.32 (br d, J=12.5 Hz, 2α-H), 9.46 (s, MeO).

Presumably the first step of the photolysis is the isomerization of the conjugated enones (I and II) to the β,γ-unsaturated derivatives, which undergo further photo-induced reactions; a) α-cleavage followed by H-shift affording the ketenes which furnish the methyl esters (III and VII) or b) allylic γ-H abstraction followed by cyclization[4)] to give the cyclobutanols (IVa, Va, VIII, and IX). In fact Matsui et al.[5)] reported the isolations of two cyclobutanols, without mention of their stereochemistry, from the product of the photolysis of isopulegone, a β,γ-unsaturated derivative of II. A similar cyclobutanol was also obtained from methylisopulegone.[6)] There are examples of the photochemical formations of cyclobutanols from α,β-unsaturated ketones,[7)] in which double bond migrations are not included. The mechanism of the formation of the methyl ethers (VI and X) is uncertain yet.

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(Received March 18, 1972)