

PHOTOCYCLOADDITION REACTION BETWEEN 3-METHYLCYCLOHEXENONE  
AND 2-HYDROXY-3-METHYLCYCLOPENTENONE.

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(Received in Japan 7 July 1973, received in UK for publication 21 August 1973)

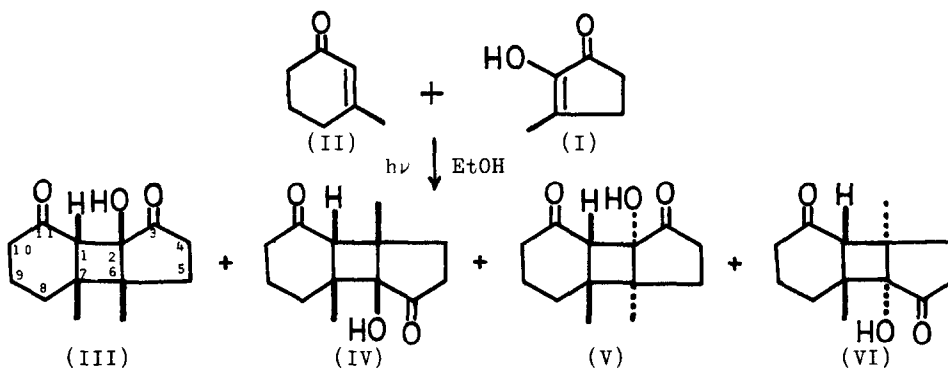
Photochemical reactions between  $\alpha,\beta$ -unsaturated ketones and olefines have been reported by many workers.<sup>1</sup> The photo-dimerization of cyclohexenone and cyclopentenone derivatives to form the cyclobutane ring has also been reported.<sup>2</sup> Produced several dimers, two of which were assigned to be head-to-head (HH) and head-to-tail (HT) adducts.<sup>3,4</sup> Very recently Mark *et al.*<sup>5</sup> reported that irradiation of 2-hydroxy-3-methylcyclopentenone (I) with a mercury lamp yielded only one HH cis-anti-cis adduct. However, there are few reports on photocycloaddition reactions between dissimilar  $\alpha,\beta$ -unsaturated ketones<sup>6</sup>

We attempted synthesis of some phytotoxic trichothecane group sesquiterpenes, which have characteristic vicinal tertiary methyl substituents on the skeletal framework. Photocycloaddition reactions between 3-methylcyclopentenone and 3-methylcyclohexenone derivatives are expected to form dimethyl-tricyclo[5.4.0.0<sup>2,6</sup>]-undecane derivatives. If the reaction occurs head-to-head, followed by retro-aldol cleavage of the cyclobutane ring, it may yield desired compounds having vicinal tertiary dimethyl substituents

Therefore, the photocycloaddition reaction between 2-hydroxy-3-methylcyclopent-2-en-1-one (I) and 3-methylcyclohex-2-en-1-one (II) was investigated. A solution of I (5.05 g) and II (4.95 g) in ethanol (150 ml) was irradiated with the Ushio UM-102 100W high-pressure mercury lamp through a pyrex filter jacket. The reaction mixture was stirred by blowing dry nitrogen gas at 15-20° for 10 days. The reaction products were separated by chromatography on silica gel (Wako-C-200). Elution with benzene acetone (200 l) gave a 1:1 mixture of III and IV (0.45 g; 4.5 %). Fractional crystallization from benzene afforded III, mp. 167.5-168.5°, and

IV, mp. 147-147.5°. The following elution with benzene:acetone (100:1) gave V, (0.98 g; 9.8%) mp. 94.5-95.5°. Further elution with benzene acetone (50:1) gave VI (0.31 g; 3.1%), mp. 265-267°. A small amounts of the dimers of I and II were detected from the reaction mixture.

The compounds III-VI showed the same molecular ion peak  $[M]^+$  at 222 in their mass spectra and the elemental analytical values. IR spectra of III-VI showed absorption bands of the hydroxyl, five and six membered carbonyl groups. Also observed two singlet methyl protons and a singlet proton of the cyclobutane ring in their NMR spectra. From these data, the structures of III-VI were assumed to be dimethyl-dioxo-tricyclo[5.4.0.0<sup>2,6</sup>]undecanol of the 1:1 adduct of I and II.



Treatment of III-VI with p-toluenesulfonic acid in benzene did not cause epimerization and unchanged starting materials were recovered, but V gave triketone by cleavage of the cyclobutane ring. These facts show that the geometry of the ring fusion of six and four membered rings have a cis based on the information of the bicyclo[4.2.0]octan-2-one systems.<sup>7</sup>

In order to determine the structures and stereoformula of III-VI we have undertaken NMR spectrometry. In the compound V, OH proton appeared lower field at  $\delta$  4.50 than the other compounds, and also IR spectrum of V showed strong absorption band at  $\nu$  3468  $\text{cm}^{-1}$  in dil carbon tetrachloride solution ( $1.35 \times 10^{-4}$  M), which were suggested intramolecular hydrogen bonding. However, the original NMR spectra of III-VI (in  $\text{CDCl}_3$ ) could not allow us to determine their structures.

The NMR spectra of III-VI were also measured in deuteropyridine for examine the structures by solvent effects, which are shown in the Table. Two methyl signals of III and IV are shifted lower field, while V and VI are shifted higher

Table The chemical shift of two methyl groups of III-VI in  $\text{CDCl}_3$  and  $d_5$ -pyridine ( $\delta$ , ppm)

	III		IV		V		VI	
$\text{CDCl}_3$	0.87	1.25	1.09	1.22	0.92	1.33	0.98	1.04
$d_5$ -pyridine	0.96	1.26	1.25	1.36	0.89	1.02	0.87	0.98
$\Delta\delta$	+0.09	+0.01	+0.16	+1.14	-0.03	-0.31	-0.11	-0.06

field. The results suggested have similar stereoformula III and IV, and V and VI, respectively.

Then, NMR spectra were measured with addition of tris(dipivaloylmethanato)-europium,  $\text{Eu(DPM)}_3$ , as chemical shift reagent,<sup>8</sup> but the spectrum of V could not be measured due to decomposition of the shift reagent. In Figure 1a-c are shown these shift curves of their  $\delta$  values for several concentrations of  $\text{Eu(DPM)}_3$  in a deuteriochloroform solution of III, IV, and VI. The two tertiary methyl protons and a proton of the cyclobutane ring moved lower field due to nearly distance from the hydroxyl group, which were accommodated from the Fig. 1a-c.

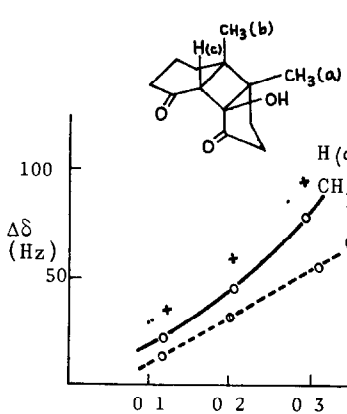


Fig. 1a

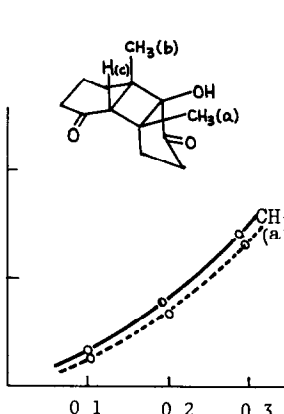
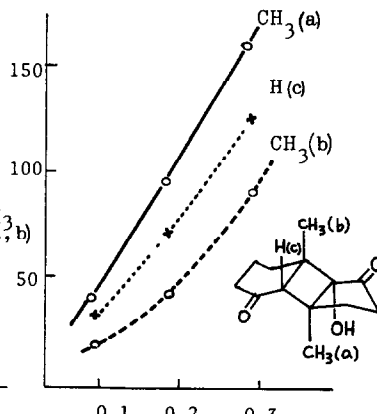


Fig. 1b

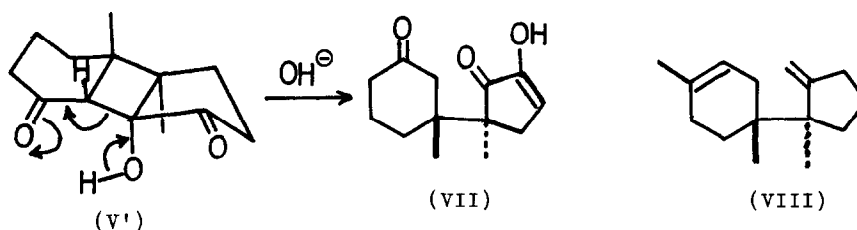
Fig. 1c  $[\text{Eu(DPM)}_3]/[\text{Substrate}]$ 

From the above NMR spectrometric investigations supported the stereochemical assignment shown in III (HH, cis-syn-cis), IV (HT, cis-syn-cis), V (HH, cis-anti-cis), and VI (HT, cis-anti-cis).

Therefore, the retro-aldol reaction of V is expected to form a desired vicinal dimethyl compound. Treatment of V with 10% KOH gave a crystalline product (VII), mp. 128-128.5°. [MS: m/e 222  $[\text{M}]^+$ ; UV:  $\lambda_{\text{max}}^{\text{EtOH}}$  257 nm ( $\epsilon$  7600) (enolic  $\alpha$ -diketone); IR  $\nu_{\text{OH}}$  3370,  $\nu_{\text{C=O}}$  1703, 1685,  $\nu_{\text{C=C}}$  1645  $\text{cm}^{-1}$ ; NMR.  $\delta$  6.48 (triplet,

$J=3$  Hz; vinyl), 6.06 (singlet; OH), 0.94 and 1.15 (singlet, methyl)] The ferric chloride color test of VII show positive. The structure of VII to be shown 2-hydroxy-5-methyl-5-(1-methyl-3-oxocyclohexyl)cyclopentenone (VII) by the above spectral data

Conversion studies of VII toward to tricodiene (VIII)<sup>9</sup> are now in progress.



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