September, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 2725—2726 (1985)* 2725

Synthetic Photochemistry. XXXII.[1] Structures of By-products Formed in the Photocycloaddition of Myrcene to Methyl 2,4-Dioxoalkanoates

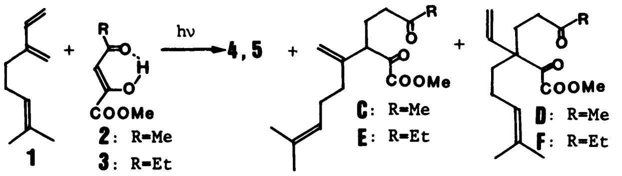
Hitoshi Takeshita,* Kei Komiyama,† and Koya Okaishi†
Research Institute of Industrial Science, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816
†*Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816*

(Received April 2, 1985)

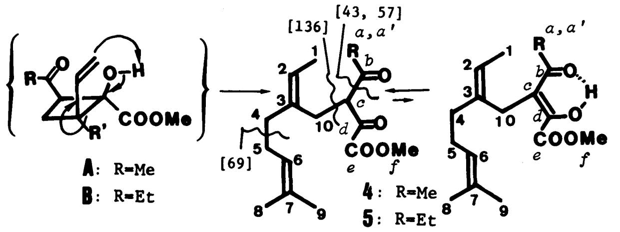
Synopsis. Structures of the by-products formed in the photocycloaddition of myrcene to methyl 2,4-dioxohexanoate and 2,4-dioxopentanoate were elucidated. They were shown to be formed by a 1,5-hydrogen shift of the intermediate $(2+2)\pi$ adducts of conjugated dienes.

In the course of the photocycloaddition studies regarding myrcene (**1**), a conjugated monoterpene diene, to methyl 2,4-dioxopentanoate (**2**)[1] and to methyl 2,4-dioxohexanoate (**3**),[2] we have isolated a hitherto unknown mode of by-products which were derived from the protoadducts (**A** and **B**) of the $(2+2)\pi$ adducts (**C**—**F**). This paper will describe the determination of their structures.

The reaction of **1** with **2** afforded a minor product (**4**) in a 20% yields when irradiation was performed between 0 and 5 °C. Since the photocycloaddition of **2** with olefins gives preparatively useful 1,5-diketones in good yields with a highly *regio*-selective fashion, an investigation of such by-product formation should be important. The molecular-weight determination of **4** by the mass spectrum[3] was confirmed to be a 1:1-adduct; *m/z*, 280 (M^+). Among its fragment ions, the acetyl group (*m/z*, 43), the base peak, and another prominent peak due to $C_{10}H_{16}$-moiety (*m/z*, 136) were suggestive. An alternative possibility of $C_9H_{12}O$ for the latter peak was eliminated by the appearance of the same fragment in the mass spectrum of a similar product (**5**) derived from **1** and **3**. In addition, another strong peak due to C_5H_9-ion (*m/z*, 69) ascribable to a 3-methyl-2-butenyl (prenyl) fragment appeared in both the spectra of **4** and **5**. Therefore, they are composed of two moieties, an intact C_{10}-framework of myrcene and the dioxoalkanoate group, linked with one C–C bond.



Scheme 1.



Scheme 2.

The NMR spectra[4] of **4** and **5**, respectively, exhibited not only the presence of acyl groups together with an oxalyl group [δ=2.20(3H, s) for **4** and 1.02(3H, t, J=7 Hz) and 3.83(2H, q, J=7 Hz) for **5**], but also signals ascribable to three methyl groups on the sp^2-carbons. It is certain that the signals for the two methyls are ascribable to the original isopropylidene moiety of **1**, and the third methyl signals (d, J=7 Hz), whose spin-coupling was confirmed respectively by double irradiation experiments, indicated the formation of an ethylidene group from the vinyl group in **1** (Scheme 2). Other than those mentioned, the NMR spectra of **4** and **5** resembled each other. This indicated that their structural relationships and structures could be discussed on the same ground. The NMR spectrum of **4** showed a pair of signals, 2.58(2H, d, J=7 Hz) and 4.25(1H, t, J=7 Hz), which were ascribable to the $R_2C{=}CR{-}CH_2{-}CH(CO)_2$-group. The methine signal disappeared upon a brief treatment with deuterium oxide. At the same time, the methylene signal at 2.58 changed to a singlet. As expected, the integration of the methine, the methylene, and the methoxy methyl signals were weaker than other signals; therefore, although the iron(III) chloride test was negative (as ordinary monoalkylated β-diketone), **4** should be an equilibrated keto-enol mixture. The methylene signal at 3.27 and the methyl signal at 3.84 should be attributable to the enolic tautomer. Due to this tautomerism, the ^{13}C-NMR spectrum of **4** was quite complicated, but its spectrum could, nevertheless, be analyzed with the aid of the assignment for myrcene and citronellol (Table 1). Its spectrum disclosed three carbonyl carbons, four olefinic carbons, and another ten aliphatic carbons.

Consequently, the structure of **4** could be expressed (as shown) and the other product **5** is the propionyl homolog.

The structures of **4** and **5** suggest that their formation involves a formal *retro*-Prins reaction, that is a 1,5-hydrogen shift from the *proto*-$(2+2)\pi$-adducts (**A** and **B**) to the 2-alkanoylcyclobutanols.

The yield of **4** or **5** was improved when the irradiation was carried out at low temperatures. Between 0 and 5 °C, the yield of **4** was 22%, but at an elevated temperature (25—30 °C),[5] its formation was suppressed and became practically undetectable. On the other hand, when irradiation was carried out at −35 °C, the yield of **4** was 28%. Furthermore, yields of **4** were as low as 4.8% when the irradiation was stopped immediately after a complete consumption of the starting material. Therefore, **4** and **5** are

TABLE 1. THE ^{13}C NMR SPECTRA OF **4** AND **5** (δ IN $CDCl_3$)

No.	(**2**)[a]	Keto forms		Enol forms	
		4	**5**	**4**	**5**
1	(115.5)	13.3	13.2	13.3	13.2
2	(139.0)	120.2	119.9	122.6	122.4
3	(135.9)	134.8	134.6	136.4	136.6
4	(30.8)	30.6	30.6	27.7	27.8
5	(24.5)	25.6	26.2	26.6	26.5
6	(124.4)	123.9	124.0	123.6	123.5
7	(131.0)	131.5	131.0	131.8	131.6
8	(17.1)	17.6	17.5	17.6	17.5
9	(25.1)	26.6	26.9	14.9	25.4
10	(112.6)	26.8	16.9	36.2	37.0
a		25.6	7.3	25.6	8.1
a′			34.6		36.2
b		203.9	206.2	200.0	204.4
c		59.8	58.9	109.2	109.0
d		189.1	188.9	171.8	168.9
e		163.0	163.3	160.7	160.7
f		52.8	53.2	53.2	53.0

a) This column is included as a reference.

photochemical-reaction products from the metastable *proto*-photoadducts, **A** and **B**.

The intramolecular nature of the hydrogen shift is obvious due to its occurrence in the aprotic solvent.

In the case of the photochemical reaction of **1** with 2-methyl-1,3-butadiene (isoprene, **6**),[6] none of the *retro*-Prins product were detected. The IR spectral monitoring of the reaction suggested that the *proto*-adducts from **2** and **6** are quickly dealdolized at that temperature.

In conclusion, from the required geometry for the formation of **4** or **5**, the cycloaddition of **2** or **3** has been established to proceed *via* a geometry in which the hydroxyl and the vinyl group are *cis*. The retention of the ground-state geometry of **2**, a six-membered chelation structure, has already been proven by a chemical-structure determination of the $(4+2)\pi$-adducts of **2** with cyclopentadiene.[7]

Experimental

Photocycloaddition of 1 to 2. An EtOAc solution (20 cm^3) of **1** (300 cm^3) and **2** (500 mg) was irradiated by means of a 400-W high-pressure mercury lamp through a Pyrex glass filter between 0 and 5 °C under a nitrogen atmosphere for 8 h. Any excess **1** was then collected by distillation *in vacuo*, and the residue was chromatographed on a silica-gel column. From the least polar fractions eluted by hexane–AcOEt (9:1), a colorless oil was obtained as a mixture of three compound.[1] Subsequently, the mixture was rechromatographed on a prepacked silica-gel column by use of a System 500 apparatus, Nippon Waters, Co., to give **C**,[1] **D**,[1] and **4**, a colorless oil, 215 mg (22%) [Found: C, 68.58; H, 8.67%; M$^+$, 280.1675. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63%; M$^+$, 280.1675. ^{1}H NMR δ=1.59(3H, s), 1.63(3H, d, J=7 Hz), 1.67(3H, s), 2.0(4H, m), 2.20(3H, s), 2.30(3H, s)*,[8] 2.57(1H, d, J=8 Hz, s by add. D_2O), 3.21(2H, s), 3.81(3H, s)*, 3.84(3H, s), 4.36(1H, t, J=8 Hz), 5.00(1H, br. s), 5.36(1H, q, J=7 Hz). IR ν: 1740, 1720, 1220 cm^{-1}].

Photocycloaddition of 1 to 3. A neat mixture of **1** (25 cm^3) and **3** (500 mg) were placed in a cylindrical vessel and irradiated by means of a high-pressure mercury lamp between 0 and 5 °C for 8 h. The mixture was then distilled *in vacuo* to recover **1**, and the residue was chromatographed on a silica-gel column to give a crude photoadduct mixture.[2] Repeated chromatography of the fractions by high-pressure liquid chromatography (HPLC) on Micro-polasil with hexane–AcOEt (95:5) afforded **E**,[2] **F**,[2] and **5**, a colorless oil, 21 mg (2%) [Found: C, 69.58; H, 8.67; M$^+$, 294.1836. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90%; M$^+$, 294.1831. ^{1}H NMR δ=1.06(3H, t), 1.58(6H, s), 1.62(3H, d, J=7 Hz), 1.99(4H, m), 2.58(2H, d, J=7 Hz), 2.59(2H, q, J=7 Hz), 3.27(2H, s)*,[8] 3.83(3H, s)*, 3.85(3H, s), 4.25(1H, t, J=7 Hz), 5.05(1H, m), 5.35(1H, q, J=7 Hz). IR ν: 1740, 1720, 1225 cm^{-1}], from the least polar fractions.

Photocycloaddition of 1 to 2 at Low Temperature. When a neat mixture of **1** (2.5 cm^3) and **2** (50 mg) was externally irradiated between −35 and −30 °C, after 1 h the mixture showed a formation of **4** in 4.8% yield together with **C** and **D**, in 52.4% and 42.8% yields, according to a gas-liquid chromatographic (GLC) analysis. When the irradiation was continued for another 3 h, the mixture was shown to be **C** (45%), **D** (27%), and **4** (28%), using a GLC analysis. The repeated HPLC separation of the mixture on Micro-polasil with hexane–AcOEt (95:5) furnished analytical samples of **C** (24 mg), **D** (14 mg), and **4** (19 mg).

Photocycloaddition of to 2 between 25 and 35 °C. When the same mixture of **1** (2.5 cm^3) and **2** (50 mg) was similarly irradiated between 25 and 35 °C for 2 h, the mixture became negative to the coloration with $FeCl_3$. The HPLC of a mixture on Micro-polasil with hexane–AcOEt (95:5) gave only **C** (17 mg) and **D** (33 mg).

Photochemical Reaction of 1 with 6 at Low Temperature. Attempted Preparation of the Photochemical Ene Reaction Product. An anhydrous EtOAc solution (30 cm^3) of **2** (250 mg) and **6** (*ca.* 2 g) was irradiated by means of a high-pressure mercury lamp for 6 h at −30 °C. After the evaporation of the volatile materils *in vacuo*, the residue was chromatographed on a silica-gel column to give only two previously characterized normal photoadducts.[7]

References

1) Part XXXI: K. Okaishi, T. Hatsui, and H. Takeshita, *Kyushu Daigaku Sogo Rikogaku Kenkyuka Hokoku*, **7**, 21 (1985).

2) H. Takeshita and K. Komiyama, *Kyushu Daigaku Seisan Kagaku Kenkyusho Hokoku*, **73**, 25 (1982).

3) The mass spectra were measured by an OISG-2Model Spectrometer, JEOL..

4) The NMR spectra were measured by an FX 100 Model spectrometer, JEOL, in $CDCl_3$ solutions throughout, and the chemical shifts were expressed in δ units from the internal Me_4Si.

5) The temperature was obtained by cooling with the running tap water in the summer.

6) H. Takeshita, T. Hatsui, and T. Masuda, *Kyushu Daigaku Sogo Rikogaku Kenkyuka Hokoku*, **1**, 35 (1978); H. Takeshita, T. Hatsui, N. Kato, T. Masuda, and H. Tagoshi, *Chem. Lett.*, **1982**, 1037.

7) H. Takeshita, A. Mori, and Y. Toyonaga, *Bull. Chem. Soc., Jpn.*, **48**, 307 (1975).

8) The asterisked signals were those of the enolic isomers of **4** and **5**. Enol contents in $CDCl_3$ were *ca.* 20% for both **4** and **5**.