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The Photochemical Cycloaddition of the Enol Acetate of Dimedone to Cyclopentene

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The photochemical cycloaddition of the enol acetate of dimedone to cyclopentene yields two stereoisomers I and II of 2-acetoxy-4,4-dimethyltricyclo[6.3.0.0^{2,7}]undecan-6-one. The NMR and IR data suggest a *cis-anti-cis* configuration for I and a *cis-anti-trans* configuration for II. The NMR and IR spectra determined on III, IV and V, the $NaBH_4$ reduction products of I and II, also support these configurations. Both of the photo adducts, I and II, lose acetic acid in the presence of an alkali to give an α,β-unsaturated ketone (VI), while it undergoes retro-aldol cleavage in the presence of an acid to give 4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione (VII). A comparative study was made of the mass spectra of I, II, and VI.

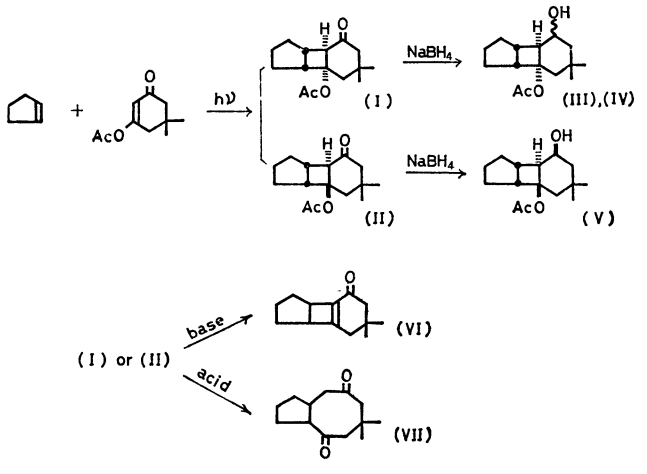
The photochemical cycloaddition of the enol acetates of β-diketones to alkenes has been reported by de Mayo *et al.*1) These photoadducts undergo retro-aldol cleavage under the basic conditions to give 1,5-diketones. Using this sequence, we undertook the photochemical cycloaddition of cyclopentene to the enolacetate of dimedone as a first step in the synthesis of terpens containing a medium-size ring. However, very few studies have been made of the stereochemistry of such photoannelation adducts. Hence, the purpose of this paper is to determine the configuration of the photoadducts. The NMR spectral data of the photoadducts thereby obtained are difficult to analyze; hence, the configuration is not easy to determine. In the present study, the configuration was determined with the aid of an NMR-shift reagent—tris(dipivalomethanato)europium,2) $Eu(DPM)_3$, which has come into use in recent years.

The product, VII, resulting from the retro-aldol cleavage of the photoadducts, I and II, has a fused ring system consisting of a five-membered ring and an eight-membered ring. Compounds of such a skeleton have rarely been synthesized thus far. They constitute a partial skeleton of some sesterterpenes and are of interest in this respect.

Results and Discussion

The enol acetate of dimedone yields, upon irradiation in cyclopentene, a mixture of two stereoisomeric photoadducts, I and II, in a ratio of roughly 2 : 1. To gain some knowledge of the configuration of such photoadducts, I and II were reduced by $NaBH_4$; I gave two alcohols, III and IV, while II gave one alcohol, V.

I or II readily loses acetic acid at room temperature to yield an α,β-unsaturated ketone (VI) upon treatment with sodium methoxide or sodium hydroxide in methanol,3) but it does not undergo retro-aldol cleavage to produce a 1,5-diketone.1) However, I or II undergoes retro-aldol cleavage in methanol containing sulfuric acid to yield a 1,5-diketone (VII).



Scheme 1.

IR Spectra of I and II. As is shown in Table 1, the I photoadduct shows a ketonic carbonyl absorption at 1703 cm^{-1} which is normal for ordinary six-membered ketones. On the other hand, the II photoadduct shows a ketonic carbonyl absorption at the unusually large wave number of 1730 cm^{-1}, which indicates the presence of a large strain in the six-membered ring of II. This finding suggests that the configuration of the ring junction between the four-membered and six-membered rings is a highly strained *trans* form in II, whereas it is *cis* in I.4)

NMR Spectra of I and II. The NMR spectra of I and II, as measured in the usual manner, do not allow the assignment of each proton because there are not large differences in chemical shift among the protons. The NMR spectra were, therefore, measured by applying $Eu(DPM)_3$ as a shift reagent.

Figure 1(a) shows the NMR spectrum of I measured in the absence of the shift reagent, while Fig. 1(b) shows the NMR spectrum of I measured in a solution of 20 mg of I in 0.4 ml of carbon tetrachloride to which 60 mg of $Eu(DPM)_3$ had been added. Likewise, Fig. 2(a) shows the NMR spectrum of II, while Fig. 2(b) shows the NMR spectrum measured in a solution of 20 mg of II in 0.4 ml of carbon tetrachloride plus 60 mg of $Eu(DPM)_3$. In both Figs. 1 and 2, the addition of 60 mg of $Eu(DPM)_3$ caused an increase in the chemical shift and a complete separation of proton signals, and the assignment of each proton was done by

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TABLE 1. IR SPECTRA OF I, II, III, IV AND V (in CCl_4)

Compound	Ester C=O	Ketone C=O	OH			
	ν (cm^{-1})	ν (cm^{-1})	ν (cm^{-1})	Intensity (%)		
				0.1 M/l	0.01 M/l	0.001 M/l
I	1740	1703				
II	1740	1730				
III	1736		3620	23	62	72
	1720 (sh)		3480—3440	77	38	28
IV	1736		3620	28	71	89
	1720 (sh)		3500—3400	72	29	11
V	1744		3580	90	89	91
	1700		3460	10	11	9

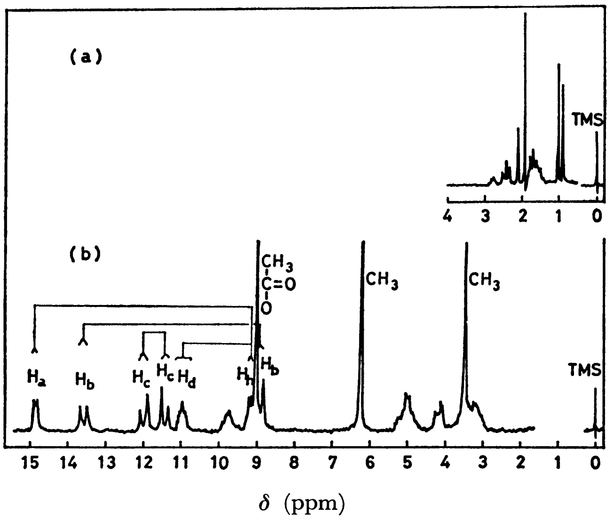


Fig. 1. The NMR spectra of I in CCl_4 (20 mg/0.4 ml) at 90 MHz (a) without Eu(DMP)$_3$ and (b) with 60 mg Eu(DPM)$_3$.

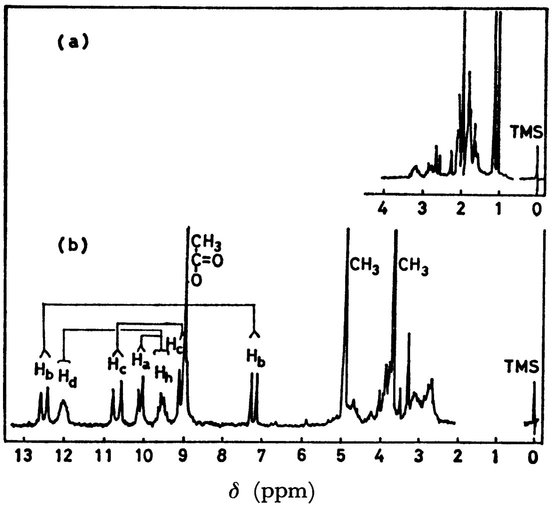


Fig. 2. The NMR spectra of II in CCl_4 (20 mg/0.4 ml) at 90 MHz (a) without Eu(DPM)$_3$ and (b) with 60 mg Eu(DPM)$_3$.

carrying out proton decoupling in this state. When the NMR spectra of I and II are measured by changing the amount of Eu(DPM)$_3$ added—that is, by adding 5, 10, 15, 20, 30, 40 or 60 mg of Eu(DPM)$_3$, the chemical

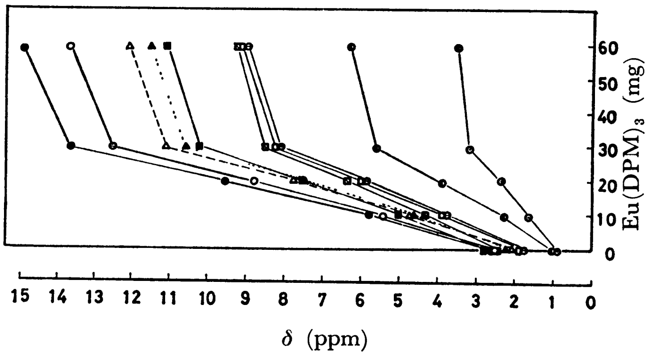


Fig. 3. Variation in chemical shift for each proton of I *vs.* the amount of added Eu(DPM)$_3$ in CCl_4 (20 mg/0.4 ml). ● H_a; ○ ⊖ H_b; △ ▲ H_c; ■ H_d; ▧ H_h; □ CH_3COO; ⊙ ◐ CH_3.

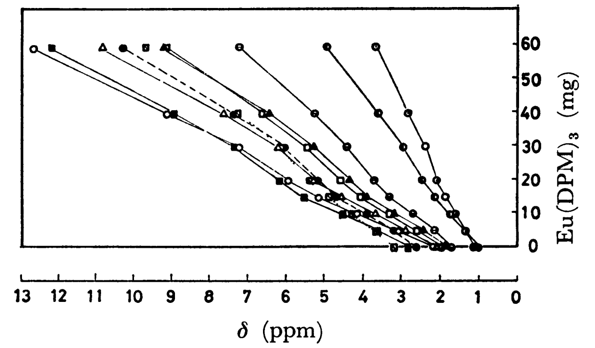


Fig. 4. Variation in chemical shift for each proton of II *vs.* the amount of added Eu(DPM)$_3$ in CCl_4 (20 mg/0.4 ml). ● H_a; ○ ⊖ H_b; △ ▲ H_c; ■ H_d; ▧ H_h; □ CH_3COO; ⊙ ◐ CH_3.

shift of each proton varies with the amount of Eu(DPM)$_3$ added in the manner shown in Figs. 3 and 4. It is hence possible to determine by interpolation the chemical shift of each proton in the absence of Eu(DPM)$_3$. The values thus obtained are shown in Table 2. The coupling constants of protons are given in Table 3.

The difference in chemical shift for each proton before and after the addition of 60 mg of Eu(DPM)$_3$, designated as $\Delta\delta$, is shown in Table 2. In the case of the addition of 60 mg of Eu(DPM)$_3$, the values of $\Delta\delta$ suggest that Eu(DPM)$_3$ forms complexes with both ketone and ester groups. A comparison of the $\Delta\delta$

Table 2. The chemical shifts of I and II with 60 mg $Eu(DPM)_3$ and without $Eu(DPM)_3$ (in CCl_4)

Compd	$Eu(DPM)_3$ (mg)	H_a		H_b				H_c			
		δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$
I	0	2.6	12.3	1.75	7.15	2.5	11.1	2.1	9.9	2.2	9.2
	60	14.9		8.9		13.6		12.0		11.4	
II	0	2.65	7.45	1.7	5.5	2.15	10.35	1.9	7.15	2.05	8.65
	60	10.1		7.2		12.5		9.05		10.7	

Compd	$Eu(DPM)_3$ (mg)	H_d		H_h		CH_3COO		CH_3		CH_3	
		δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$
I	0	2.8	8.2	2.45	6.7	1.9	7.1	1.0	5.25	0.9	2.6
	60	11.0		9.15		9.0		6.25		3.5	
II	0	2.85	9.2	3.2	6.35	1.95	7.05	1.1	2.55	1.0	3.9
	60	12.05		9.55		9.0		3.65		4.9	

(I or II; 20 mg/0.4 ml CCl_4)

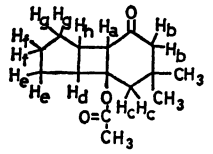


Table 3. Coupling constants

Compd	$J_{H_aH_h}$	$J_{H_bH_b}$	$J_{H_cH_c}$	$J_{H_dH_h}$
I	7 Hz	15	16	6
II	8 Hz	15	17	7

values reveals information on the configurations of I and II. As is shown in Table 2, the H_a of I has a considerably larger $\Delta\delta$ value than the H_a of II. It is likely that the proximity of H_a and –OAc in I, or a *cis* configuration as suggested by the IR data, results in a larger shift for H_a, while a *trans* configuration for H_a and –OAc in II is affected less by the shift reagent. On the other hand, the spatial relationship between H_a and the ketone carbonyl group seems not to differ from I to II. Now, the $\Delta\delta$ for the H_d of II is larger than that for the H_d of I, although the difference here is not so pronounced as in the $\Delta\delta$ for H_a. In considering the configuration of H_d and –OAc, it is likewise assumed that the shift appears larger in II because of the *cis* configuration for H_d and –OAc, while the shift is smaller in I on account of the *trans* configuration for H_d and –OAc. Moreover, H_h is little affected by the shift reagent, as it is located in the β-position relative to both carbonyl and ester groups; only a small difference in chemical shift is found between I and II.

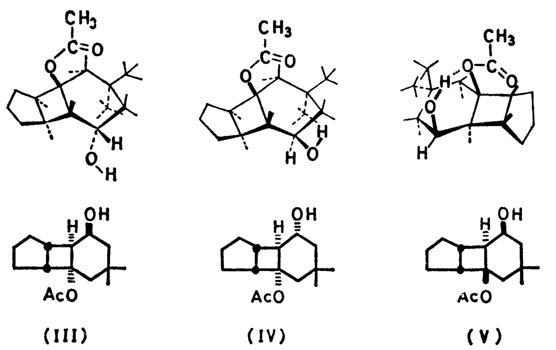
In the NMR spectra measured in the absence of the shift reagent, I shows the chemical shift of H_h at a normal value of $\delta=2.5$, while II shows it in an unusually low magnetic field of $\delta=3.2$. The configuration for H_h and –OAc is *cis* in II; that is, H_h is nearer to the ester carbonyl group. The anisotropy[5)] of this ester carbonyl group seems to account for the appearance of the chemical shift of H_h in the lower magnetic field. On the contrary, the lack of such a phenomenon in I suggests that H_h and the ester group in I are not *cis* to each other.

In summary, the above-mentioned results indicate that I assumes a *cis-anti-cis* configuration, while II assumes a *cis-anti-trans* configuration. The fusion of the five-membered and four-membered rings is *cis* in both I and II.

IR Spectra of III, IV, and V. The infrared spectra were measured on the III, IV, and V alcohols which had been obtained from I and II by reduction with $NaBH_4$ in order to determine whether or not there was an intramolecular hydrogen bond between the alcoholic OH and the carbonyl oxygen or ether oxygen of the ester group. The measurements were made in carbon tetrachloride at concentrations of 0.1, 0.01, and 0.001 mol/l. The absorptions due to OH stretching look alike in III and IV. As is shown in Table 1, the alcohol, III or IV, arising from the reduction of I produces an absorption peak due to free hydroxyl at 3620 cm^{-1} and a broad absorption peak due to the hydrogen-bonded hydroxyl group near 3500 cm^{-1}; the relative intensity of these peaks varies with the concentration. The absorption near 3500 cm^{-1} becomes exceptionally strong at high concentrations (0.1 mol/l), but it weakens as the concentration diminishes. This indicates that the absoption near 3500 cm^{-1} is due to an intermolecular hydrogen bond. On the other hand, the compound, V, which has been obtained by the reduction of II shows a strong and sharp absorption peak at 3580 cm^{-1} and a weak but sharp absorption peak at 3460 cm^{-1}, and the relative intensity of these two peaks is not affected at all by the concentration in the range from 0.1 to 0.001 mol/l. It is, therefore, likely that these two absorptions are due to intramolecular hydrogen bonding.

Corresponding to these OH absorptions, V shows an absorption of ester carbonyl at 1744 cm^{-1}, as is shown in Table 1. This peak is shifted towards the larger-wave-number side from 1740 cm^{-1}, where the ester carbonyl absorption of II appeared before reduction. It is known that hydrogen bonding between OH and ester carbonyl shifts the infrared absorption of the carbonyl towards the smaller-wave-number side, while hydrogen bonding between OH and ether oxygen of the ester group shifts it towards the larger-wave-number side.[6] It is, therefore, assumed that the principal hydrogen bond of V (OH absorption at 3580 cm^{-1}) gives rise to a six-membered ring involving the OH and ether oxygen of the ester group. The carbonyl absorption of V has a shoulder at 1700 cm^{-1} which seems to be due to some contribution from a hydrogen bond between OH and ester carbonyl (the formation of an eight-membered ring); the weak but sharp OH absorption at 3460 cm^{-1} is likely to correspond to such a hydrogen bond.

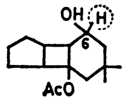
Let us suppose that II assumes a *cis-anti-trans* configuration as has been mentioned above. The six-membered ring would then be in the chair form and hydride would attack a less hindered site in the NaBH$_4$ reduction to produce only an alcohol with a configuration such as V. The construction of a molecular model shows that the OH group is axial and comes very close to the ether oxygen of the -OAc group to facilitate formation of an intramolecular hydrogen bond. On the other hand, if one assumes a *cis-anti-cis* configuration for I, the six-membered ring would not be in the chair form, but rather, in the boat form or labile form, and hydride would attack the carbonyl group from both sides in the NaBH$_4$ reduction to yield two alcohols, III and IV. Molecular models of III and IV show that the OH group and the ester group are sufficiently separated to make the formation of an intramolecular hydrogen bond impossible.



Scheme 2.

NMR Spectra of III, IV, and V. The NMR spectra of III, IV, and V, like those of I and II, do not show much differences in chemical shift, and the definite assignment of each proton is not possible. However, the proton linked to the carbon carrying the OH group can be distinguished because its signal appears in lower magnetic fields than the other protons. Table 4 shows the chemical shift and the half-width (W$_{1/2}$) of this signal. When three or more protons are present on neighboring carbon atoms, as in -CH$_2$-CH(OH)-CH<, the proton on the carbon atom carrying the OH group has a larger coupling constant and, hence, ordinarily a larger half-width of the signal in the axial conformation than in the equatorial conformation —in general, 16 Hz or more in the axial conformation and 12 Hz or less in the equatorial conformation.[7] If this is applied to III, IV, and V, the proton in question is equatorial in III and V and axial in IV, as is shown in Table 4. These results agree with those obtained from the IR data on V mentioned above and support the configuration of V.

TABLE 4. THE NMR SIGNALS FOR 6-HYDROGEN OF III, IV, AND V



Compd	δ	W$_{1/2}$ (Hz)	Conformation of 6-hydrogen
III	3.77	9	equatorial
IV	4.05	18	axial
V	4.01	10	equatorial

TABLE 5. THE RATE CONSTANTS OF I AND II→VI AT 25 °C

Comp.	Initial concentration a=[NaOH] (mol/l)	k (s^{-1})
I	8.40×10^{-5}	8.87×10^{-5}
II	8.34×10^{-5}	2.25×10^{-4}

Rate of Formation of α,β-Unsaturated Ketone (VI) from I or II. I or II loses acetic acid in an alkaline solution to yield an α,β-unsaturated keton (VI). The rate of this reaction was determined in ethanol at 25 °C. An ethanol solution of sodium hydroxide was used as an alkali. The reaction is first-order, and a plot of $\log(a-x)$ against t gave a linear relationship wherein a is the initial concentration of I or II, x is the amount of VI formed, and t is the reaction time. The rate constant, k, obtained from the slope of this straight line is given in Table 5.

The rate constant, k, in this case varies with the concentration of alkali. Since the alkaline concentration is the same for I and II, equal to the initial concentration of I or II, the k for II is about 2.7 times as large as that for I. In general, the ionic elimination reaction proceeds more readily in a *trans* configuration than in a *cis* configuration; this also supports the idea that the ring fusion of the four-membered and six-membered rings is *trans* in II and *cis* in I.

Any of the above-mentioned results indicates that I has a *cis-anti-cis* configuration, while II has a *cis-anti-trans* configuration.

Mass Spectra of I, II, and VI. The mass spectra of I and II are shown in Figs. 5(a) and 5(b) respectively. Neither shows any molecular peak corresponding to m/e=250 indicating a cleavage of the cyclobutane ring. On the other hand, the elimination of acetic acid also takes place. In particular, II shows a mass spectral pattern similar to that of the α, β-unsaturated ketone (VI) shown in Fig. 5(c), signifying a ready occurrence of the elimination of acetic acid. I undergoes the elimination of acetic acid only slightly, about 1/20 as much as II; it primarily suffers a cleavage of the cyclobutane ring.

The principal fragment ions and estimated fragmentations are shown below. A metastable peak is observed at m/e=108.8; this indicates the formation of a fragment ion of m/e=141 from a fragment ion of

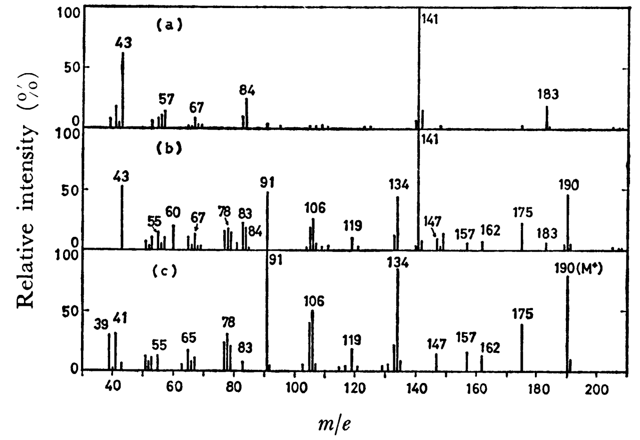
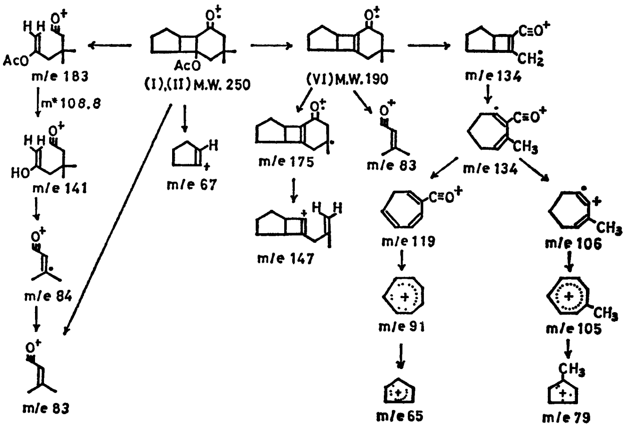


Fig. 5. Mass spectra of I, II and VI. (a) I; (b) II; (c) VI.



Scheme 3.

$m/e = 183$.

Experimental

The NMR spectra were determined on a Hitachi R-22 spectrometer at 90 MHz, with TMS as the internal standard. The mass spectra measured with a Hitachi RMU-6L and RMU-7M spectrometer. The IR spectra were recorded with a JASCO IR-G spectrophotometer. The UV data were recorded with a Hitachi EPS-3 spectrophotometer. The VPC analyses were carried out on a 063 Hitachi gas chromatograph. The melting points were uncorrected.

2-Acetoxy-4,4-dimethyltricyclo[6.3.0.0^{2,7}]undecan-6-one (I and II). A solution of 16.5 g of dimedone enol acetate in 200 ml of cyclopentene was irradiated for 15 h in a Pyrex tube with a 100-W high-pressure marcury arc at 0—5 °C in a nitrogen atmosphere. The crude crystalline residue remaining after the removal of the solvent was crystallized from ether; 14.4 g were thus yielded as a mixture of I and II (65% yield). Fractional recrystallization from ether afforded 7 g of I and 3.2 g of II.

I: mp 126—127 °C. IR (see Table 1). NMR (see Fig. 1 and Table 2). Found: C, 71.76; H, 8.80%. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86%. MS (see Fig. 5(a)).

II: mp 117—118 °C. IR (see Table 1). NMR (see Fig. 2 and Table 2). Found: C, 72.04; H, 8.24%. MS (see Fig. 5(b)).

Sodium Borohydride Reduction of I. A solution of 1 g of the I adduct in 20 ml of methanol was stirred, over a 5-min period, into a solution of 0.1 g of sodium borohydride in 10 ml of methanol at 0—5 °C. The mixture was kept in an ice bath for 25 min, diluted with 150 ml of water, and extracted with ether (three times). The evaporation of the extract after drying gave an oily mixture of III and IV (1 g). VPC analysis indicated that the mixture consisted of 66% III and 34% IV. Repeated fractional crystallizations from hexane gave the pure III and IV.

III: mp 49.5—51.5 °C. IR (see Table 1). NMR ($CDCl_3$): δ 0.98 (3H, CH_3), δ 1.02 (3H, CH_3), δ 2.00 (3H, $OCOCH_3$) and δ 3.77 (m, 1H, $C\underline{H}OH$). Found: C, 71.22; H, 9.60%. Calcd for $C_{15}H_{24}O_3$: C, 71.43; H, 9.52%

IV: mp 86—88.5 °C. IR (see Table 1). NMR ($CDCl_3$): δ 0.88 (3H, CH_3), δ 0.94 (3H, CH_3), δ 1.98 (3H, $OCOCH_3$) and δ 4.05 (m, 1H, $C\underline{H}OH$). Found: C, 71.38; H, 9.27%.

Sodium Borohydride Reduction of II. The II adduct (1 g) was reduced by the method described above. The yielded product showed one peak in VPC and one spot in TLC. The crystallization from hexane gave 0.82 g of V (82% yield). Mp 54.5—55.5 °C (after four recrystallizations). IR (see Table 1). NMR ($CDCl_3$): δ 0.97 (3H, CH_3), δ 1.14 (3H, CH_3), δ 2.07 (3H, $OCOCH_3$) and δ 4.01 (m, 1H, $C\underline{H}OH$). Found: C, 71.56; H, 9.34%. Calcd for $C_{15}H_{24}O_3$: C, 71.43; H, 9.52%.

4,4-Dimethyltricyclo[6.3.0.0^{2,7}]-$\Delta^{2,7}$-undecen-6-one, VI (α,β-Unsaturated Ketone). A solution of 5.9 g of photoadducts (mixture of I and II) in 65 ml of absolute methanol was stirred into a solution of sodium methoxide, prepared from 0.6 g of sodium and 50 ml of absolute methanol. The mixture was then allowed to stand at room temperature overnight. The methanol was removed under reduced pressure after neutralization with Dry Ice. The remaining oil was extracted with ether. The ethereal extract was washed with water and dried by sodium sulfate. The subsequent removal of the solvent gave 3.7 g of a pale yellow oil. After distillation, 2 g of a colourless oil was obtained (44% yield). A solution of 1.1 g of I in 50 ml of absolute methanol, in which there was dissolved 0.2 g of sodium, was allowed to stand overnight; 0.61 g of the α,β-unsaturated ketone was thus obtained (76% yield). The 0.2 g of II also produced 0.08 g of VI (53% yield); bp 136—138 °C/14 mmHg; mp 24—25 °C (after three distillations). IR: 1660 cm^{-1}, UV (ethanol): 250 nm (ε, 9250) and 322 nm (ε, 98). Found: C, 82.35; H, 9.12%. Calcd for $C_{13}H_{18}O$: C, 82.11; H, 9.47%. MS (see Fig. 5(c)). 2,4-DNP: mp 173—174 °C.

4,4-Dimethylbicyclo[6.3.0]undecane-2,6-dione, VII. A solution of 1 g of I in 50 ml of methanol containing 1.5 ml of sulfuric acid was left to stand for two weeks at room temperature. The reaction mixture was then concentrated under reduced pressure and extracted with ether. The ethereal extract was neutralized with sodium bicarbonate, washed with water, and then dried over sodium sulfate. The semicrystalline residue remaining after the removal of the ether was sublimed under reduced pressure (13 mm Hg) to give 0.46 g of the dione, VII (56% yield). Also, 1 g of II produced 0.41 g of VII (50% yield). Crystallization from hexane afforded pure crystals; mp 64—65 °C. IR (Nujol) 1695 cm^{-1}. NMR ($CDCl_3$): δ 1.11 (3H, CH_3) and δ 1.13 (3H, CH_3). Found: C, 75.14; H, 9.60%. Calcd for $C_{13}H_{20}O_2$: C, 75.00; H, 9.62%. MS: m/e 208 (M^+, $C_{13}H_{20}O_2$, 5%), 193 ($C_{12}H_{17}O_2$, 5), 190 ($C_{13}H_{18}O$, 11), 180 ($C_{12}H_{20}O$, 4), 152 ($C_9H_{12}O_2$, 13), 141 ($C_8H_{13}O_2$, 26), 124 ($C_8H_{12}O$, 41), 112 ($C_7H_{12}O$, 24), 95 (C_6H_7O, 43), 83 (C_5H_7O, base), 81 (C_6H_9, 23), 67 (C_5H_7, 29), 55 (C_4H_7, C_3H_3O, 24) and 41 (C_3H_5, 23).

Determination of the Rate Constants (I and II→VI). The rate of the elimination reaction of acetic acid (I or II→VI) was followed spectrophotometrically at the absorption maximum of 250 nm.

The solutions of I (2.80×10^{-3} mol/l), II (2.78×10^{-3} mol/l), and sodium hydroxide (8.01×10^{-3} mol/l) in ethanol were each thermally equilibrated at 25 °C. To a 100-ml volumetric flask, 3 ml of a solution of I or II was added, after which the solution was diluted with ethanol (equilibrated at 25 °C) to a volume of nearly 89 ml. Then an equimolar portion of sodium hydroxide solution was added to the flask (1.05 ml for I and 1.04 ml for II), and finally the mixture was diluted to 100 ml with ethanol. The flask was placed in a thermostatic bath at 25 °C. Suitable aliquots of the sample solution were withdrawn at 10—30 min intervals, and immediately the absorbance was measured against an ethanol blank at 250 nm. The concentration of VI (x) was calculated from its extinction coefficient (ε, 9250). In these experiments, the initial concentration of I was 8.40×10^{-5} mol/l, and that of II was 8.34×10^{-5} mol/l. The results are shown in Table 5.

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