of the cumulene and the aromatic protons. The solutions of all ketenimines **1** were stable under the conditions of the kinetic experiments.

Solvents were purified by standard methods[16] and stored under an argon atmosphere.

Kinetic Measurements. (a) UV Method. This method was employed for the study of the 1,4-cycloaddition reactions. Exact amounts (2–3 mL) of ketenimine and thioketone solutions were mixed in a Pyrex ampule whose path length (ca. 1.4 cm) had been precisely determined by standard solutions of thiobenzophenone (**2a**). The solution was quickly frozen and then degassed by the freeze–thaw technique under vacuum (0.001 mmHg). Finally, the ampule was sealed and positioned in the thermostated (±0.2 °C) cell compartment of a Perkin-Elmer Model 402 UV spectrophotometer. The kinetics were followed by monitoring the thioketone through its absorbance in the visible region (590–650 nm). Reactions were followed to at least 2 half-lives, and rate constants were calculated from the second-order rate equation.

(b) ^{1}H NMR Method. This method was employed for the study of the 1,2-cycloaddition reactions. The solution (0.5 mL) of the ketenimine was added to a weighed amount of thioketone in a NMR tube, and the mixture was frozen and degassed by the usual freeze–thaw technique. The NMR tube was sealed and then positioned in the thermostated (±0.3 °C) probe of a JEOLCO-60 NMR spectrometer. The reactions were followed up to 70–80% of their extent by measurement at intervals of the intensities of appropriate signals of the ketenimine, I_k, and cycloadduct, I_c, and the percentages of unreacted ketenimine were calculated from the relationship $[I_k/(I_k + I_c)]100$. The analytical peaks were those corresponding to the olefinic proton for the reactions of **1h**, **1f**, and **1g** and the methyl of the cumulene for the reaction of **1d**. The measurement of the intensity of each signal was repeated three or four times, and the values were averaged. From the percentages of unreacted ketenimine determined at different intervals and the initial amounts of the two reactants, their molar concentrations were obtained. The rate constants were calculated from the second-order rate equation.

The activation parameters were calculated by standard methods:[17] E_a from the linear plot of log A vs. $1/T$, log A from E_a through the Arrhenius equation, $\Delta S^{\ddagger}$ from log A by the equation $\Delta S^{\ddagger} = 4.576(\log A - 13.23)$, $\Delta H^{\ddagger}$ from the approximation $\Delta H^{\ddagger} = (E_a - RT)$, and $\Delta G^{\ddagger}$ $(\Delta H^{\ddagger} - T\Delta S^{\ddagger})$.

Acknowledgment. The part concerning the kinetic study of this work has been carried out at the Laboratory of the CNR of Ozzano Emilia with collaboration between this institution and A.D.

Registry No. 1b, 63086-85-1; **1d**, 74331-60-5; **1f**, 74331-61-6; **1g**, 45813-90-9; **1h**, 14181-75-0; **1n**, 14016-34-3; **1o**, 18779-86-7; **1p**, 14016-32-1; **1q**, 74331-62-7; **2a**, 1450-31-3; **2b**, 1141-08-8; **2c**, 3705-95-1; thioformaldehyde, 865-36-1; ketenimine, 17619-22-6.

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[16] A. Weissberger, "Techniques of Organic Chemistry", Vol. VII, Interscience, New York, 1955.

[17] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1941, Chapter 6.

Metal-Catalyzed Organic Photoreactions. Titanium(IV) Chloride Catalyzed Photoreaction of Saturated Ketones with Methanol and Its Application to the Synthesis of Frontalin[1]

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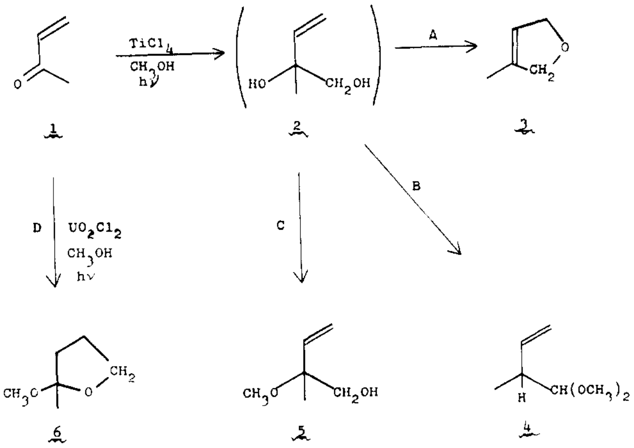
Photoreaction of acyclic and cyclic saturated ketones in methanol in the presence of $TiCl_4$ afforded 1,2-diols as the main products. The effect of the substituents on the stereochemical course of the photoreaction was examined with substituted cyclohexanones. Further, the present reaction was applied for the synthesis of a pheromone, frontalin.

We reported[2] that α,β-enones, when irradiated in alcohols in the presence of $TiCl_4$ or UO_2Cl_2, undergo novel types of reaction with the formation of a C–C bond between the substrate and alcohol. As a typical example, the $TiCl_4$- and UO_2Cl_2-catalyzed reactions of α,β-enones **1** with methanol are shown in Scheme I. Depending upon the types of the substrates, the $TiCl_4$-catalyzed photoreaction gave three types of product: dihydrofurans **3** (type A), acetals **4** (type B), and 1,2-diol monomethyl ethers **5** (type C). All the products are considered to be derived from a common intermediate, 1,2-diol **2**, which is formed through the 1,2-addition of methanol to the carbonyl group. When UO_2Cl_2 was used as catalyst, on the other hand, the products were cyclic acetals **6** (type D), derived through 1,4-addition of methanol to the enones.

Scheme I



All the reactions (types A–D) can be shown schematically to involve a step of the formal coupling of the hydroxymethyl radical with the carbonyl carbon (1,2 type) or the olefinic β-carbon (1,4 type) of the enones. However, the present reaction is characteristic in several features.[2] (1) 1,2-Addition of methanol to enones as observed in the

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[1] Preliminary report: T. Sato, S. Yamaguchi, and H. Kaneko, *Tetrahedron Lett.*, 1863 (1979).

[2] T. Sato, S. Yoshiie, T. Imamura, K. Hasegawa, M. Miyahara, S. Yamamura, and O. Ito, *Bull. Chem. Soc. Jpn.*, **50**, 2714 (1977).

0022-3263/80/1945-3778$01.00/0

$TiCl_4$-catalyzed reaction is quite unusual. It is known that most of the alcohol or ether additions to enones through the use of UV irradiation, if they ever proceed, give 1,4-type products. (2) Although hydrogen abstraction by a ketone from an alcohol is well-known, cross coupling to form a mixed pinacol is rare, ketyl–radical dimerization being usually preferred. (3) The reactivities of alcohols with ethyl 2-butenoate in the benzophenone-sensitized coupling reaction have been reported to increase in the order methanol < ethanol < 2-propanol, while the order of the reactivities of the alcohols in the present reaction was found to be completely reversed. These observations induced us to propose a mechanism other than that involving radical species, and we have suggested[2] a mechanism (Scheme II) comprising of (1) a metal-assisted and photoassisted electron transfer from the alcohol to the carbonyl compound within the coordination sphere of the metal ion, (2) the succeeding proton transfer from the alcohol radical cation to the enone radical anion, imparting a radical character to the α-carbon atom of the alcohol and the carbonyl carbon atom or the β-carbon atom of the enone, and (3) the coupling of the radicals to form a new C–C bond. All these processes are considered to be proceeding consecutively in a close vicinity on the metal ion, thus providing a circumstance favorable for the cross coupling. Evidence for this type of electron transfer among ligands on a metal ion was recently obtained, and the details of the mechanism, which we termed as a "long-range electron-transfer mechanism" have been discussed in another publication.[3] It is assumed that titanium ion coordinates strongly with carbonyl oxygen, thus favoring the 1,2-addition, while uranyl ion coordinates to π-system more effectively, and induces the 1,4-addition. We ascribed the order of reactivities of methanol > ethanol > 2-propanol to the favorable coordination of the smaller alcohols to the metal ion due to the steric effects. We wish to report here on the extension of the reaction to saturated ketones and on its application to the synthesis of a pheromone, frontalin.

Scheme II

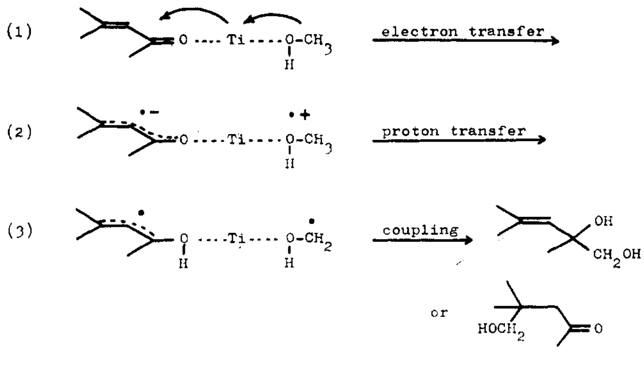
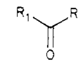
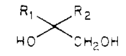
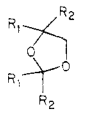
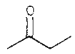
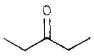
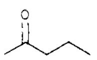
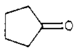
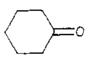
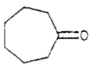
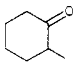
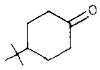
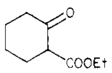
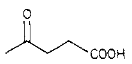
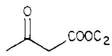


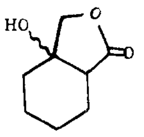
Table I. $TiCl_4$-Catalyzed Photoreaction of Ketones with Methanol

		product yield, %	
	starting ketone  7	 8	 9
a		54	
b		55	
c		68	
d		35	
e		46	20
f		35	
g		42[a]	26
h		48[b]	19
i		c	
j		d	
k		e	

[a] A mixture of cis and trans isomers (76:24). [b] A mixture of cis and trans isomers (69:31). [c] *cis*-**10** (4%), *trans*-**10** (19%), *cis*- + *trans*-**11** (24%), and **12** (16%). [d] **13** (56%). [e] **14** (~60%).

Results and Discussion

When saturated ketones **7a–h** were irradiated in methanol in the presence of $TiCl_4$, 1,2-diols **8a–h** were obtained as main products (Table I). The other ketones **7i–k** afforded products **10–14**, as shown in the Table I. It may



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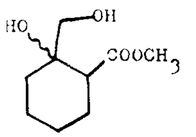

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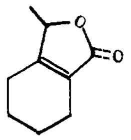

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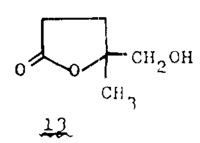

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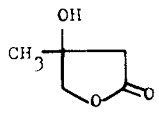

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be assumed that the products **10–14** resulted via the intermediacy of the corresponding 1,2-diols formed through the same type reaction as in cases of **7a–h**. In some cases, ketals **9** were also isolated as byproducts, which might result from subsequent condensation of the primary products **8** with the starting ketones. Actually the ketal **9e** was obtained when a methanol solution containing **7e**, **8e**, and $TiCl_4$ was allowed to stand overnight at room temperature. The structures of the products were identified mostly from the spectroscopic data. Each reaction is fairly clean, and the amounts of other products not shown in the table are negligible, as revealed by the NMR and GLC analyses on the crude reaction mixture. In the absence of $TiCl_4$, the irradiation usually afforded a mixture of several products in small amounts.

In cases of substituted cyclohexanones **7g–i**, the products were obtained as stereoisomeric mixtures. The direct determination of the cis–trans isomer ratio of **8g** was not accomplished because attempts to separate the isomers or to analyze the stereochemistry by spectroscopic methods

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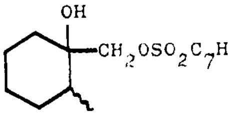
[3] E. Murayama, A. Kohda, and T. Sato, *J. Chem. Soc., Perkin Trans. 1*, 947 (1980).

were unsuccessful. Hence the ratio was estimated in the following way.

Treatment of **8g** with *p*-toluenesulfonyl chloride in pyridine gave a stereoisomeric mixture of toluenesulfonate **15**, whose NMR spectrum indicated two singlets at δ 3.81 and 3.93 in a ratio of 76:24. The separation of the stereoisomers **15** was accomplished by preparative TLC, and it was revealed by deriving each isomer to the authentic *cis* - or *trans*-1,2-dimethylcyclohexanol[4] that the signal at δ 3.81 in **15** corresponds to the cis isomer [*c*-2-methyl-1-[[(*p*-tolylsulfonyl)oxy]methyl]-*r*-1-cyclohexanol], while the signal at δ 3.93 corresponds to the trans isomer. Although the stereochemistry of the ketal **9g** was not determined, we assumed that its cis–trans isomer ratio would not greatly deviated from that in the diol **8g**, because the ketalization would not be so much affected by the stereochemical environment of **8g**. Thus we concluded that the major isomeric components in the products **8g** and **9g** are cis isomers and that the preferential course of the photoreaction is the attack by the hydroxymethyl group from the side opposite the methyl group (anti attack).



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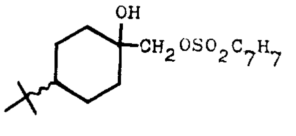

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The stereochemistry of the diol **8h** was determined in the same way as described above by converting the diols to the authentic methyl-*tert*-butylcyclohexanols[5] via the corresponding toluenesulfonates **16**, and we estimated the ratio of cis to trans isomers in the photoproducts (**8h** and **9h**) to be 69:31, again indicating the preferential anti attack of the hydroxymethyl group. These two results for the stereochemistry bear a resemblance to the results observed in the reactions of organometallic compounds with these ketones.[6]

Unlike the methyl or *tert*-butyl group, which favors the anti attack, the ethoxycarbonyl group seems to favor the syn attack. The photoreaction of 2-(ethoxycarbonyl)cyclohexanone (**7i**) gave *trans*-**10** (19%), *cis*-**10** (4%), a mixture of *cis*- and *trans*-**11** (24%), and **12** (16%). The trans structure of **10** was assigned in view of the lower field chemical shift of the proton at the ring junction (δ 2.50, t, $J = 6.3$ Hz) due to the anisotropic effect of the neighboring OH group, as compared with that of the corresponding proton in the cis isomer (δ 2.15, dd, $J = 12$, and 4 Hz). The stereochemical assignment of these isomers is also consistent with their coupling constants as observed by assuming a preferential axial conformation of the proton at the ring junction in the cis isomer. When the stereoisomeric mixture of the ester **11** was treated with dilute hydrochloric acid, trans and cis lactone **10** were obtained in a ratio of 2.2:1. These results indicate that trans isomers constitute the major part of the products in this reaction.

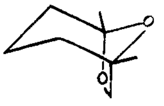
The gross stereochemical deduction from these observations is that methyl and *tert*-butyl groups function as a steric interference, thus favoring the anti attack, while ethoxycarbonyl group favors the syn attack. We attributed the preferential syn attack in the latter case to the access of titanium to the reaction site on the same side as the ethoxycarbonyl group due to the coordination to the ester group. These results would be another support for our proposal that the present photoreaction proceeds within the coordination sphere of the titanium ion.

The lactone **12** might be a product from an intramolecular reaction between the carbonyl group and the ethyl ester group, followed by dehydration. In connection with the possibility of the intramolecular reaction, we carried out the photoreaction of ethyl acetoacetate with methanol. The reaction product was a lactone, **14**, indicating that intermolecular reaction with methanol is preferable to the intramolecular reaction with the ethoxy group.

The product from **7j** was identified as γ-lactone **13** on the basis of a carbonyl band at 1760 cm^{-1} in the IR spectrum.

In view of the simple operation, high selectivity, and reasonable yields of products, the present photoreaction could be a potential technique for organic synthesis. We next applied the reaction to the synthesis of frontalin, a pheromone of the southern pine beetle *D. frontalis*.

Frontalin was first isolated by Kinzer et al. in 1969, and the structure was determined as 1,5-dimethyl-6,8-dioxabicyclo[3.2.1]octane (**17**) by the synthesis of the racemate.[7]



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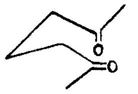

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The absolute configuration was assigned as (*S*)-(−) form by the stereoselective syntheses of the active forms.[8–12] The synthesis of the racemate has been accomplished by several workers.[7,13–15]

The synthesis of the racemate was accomplished by irradiating a methanol solution of heptane-2,6-dione (**18**) in the presence of $TiCl_4$. Almost pure frontalin (∼85% yield) was obtained by addition of water to the reaction mixture, followed by extraction with dichloromethane and evaporation of the solvent. Heptane-2,6-dione can be prepared easily from diketene and formalin,[16] so the present reaction is promising as a facile method of the frontalin synthesis. Several grams of the product can be prepared quite easily by passing the reactant solution through a quartz spiral tube which fits around a high-pressure mercury lamp (1 kW).

Experimental Section

General Procedures. The instrumentation was the same as has been described previously.[17] All the irradiations were carried out in quartz tube with 0.1 M solutions of the substrates in CH_3OH containing an equivalent amount of $TiCl_4$ by using a high-pressure mercury lamp (Ushio UM 452 (450 W)) at the temperature of

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[4] K. B. Becker and C. A. Grob, *Helv. Chim. Acta*, **56**, 2723 (1973).

[5] H. O. House and W. L. Respess, *J. Org. Chem.*, **30**, 301 (1965).

[6] T. L. Macdonald and W. C. Still, *J. Am. Chem. Soc.*, **97**, 5280 (1975); E. C. Ashby, L.-C. Chao, and J. Laemmle, *J. Org. Chem.*, **39**, 3258 (1974).

[7] G. W. Kinzer, A. F. Fentiman, Jr., T. F. Page, Jr., R. L. Foltz, J. P. Vitĕ, and G. B. Pitman, *Nature (London)*, **221**, 477 (1969).

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[13] B. P. Mundy, R. D. Otzenberger, and A. R. DeBernardis, *J. Org. Chem.*, **36**, 2390 (1971).

[14] T. D. J. D'Silva and D. W. Peck, *J. Org. Chem.*, **37**, 1828 (1972).

[15] K. Mori, S. Kobayashi, and M. Matsui, *Agric. Biol. Chem.*, **39**, 1889 (1975).

[16] R. A. Micheli, Z. G. Hajos, N. Cohen, D. R. Parrish, L. A. Portland, W. Sciamanna, M. A. Scott, and P. A. Wehrli, *J. Org. Chem.*, **40**, 675 (1975).

[17] T. Sato, K. Tamura, K. Maruyama, and O. Ogawa, *J. Chem. Soc., Perkin Trans. 1*, 779 (1976).

running water. In the reactions of cyclic ketones **7d–h**, an equivalent amount of pyridine was added in order to reduce the formation of ketals. In these cases, the irradiation was performed for 20–24 h, while in the reactions without pyridine, the irradiation time was 3–6 h. After the irradiation, the solution was poured into water and shaken with CH_2Cl_2. The extract was dried (Na_2SO_4), and the solvent was removed in vacuo. The residual substance was analyzed by GLC and spectroscopy.

Unless otherwise stated, all the spectroscopic data were determined on a sample collected by preparative GLC, a CCl_4 solution being used for the NMR and IR spectral determinations.

The yields were determined by means of NMR analyses on the crude materials described above, with tetrachloroethane as an internal reference.

The structures of the products were deduced from the following data.

8a:[18,19] mass spectrum, m/e 89 (M – 15), 87, 75, 73 (base peak), 57, 55; IR ν_{max} 3380, 2690, 2920, 2870, 1460, 1380, 1140, 1050 cm^{-1}; NMR δ 0.90 (3 H, t, J = 8 Hz), 1.09 (3 H, s), 1.48 (2 H, q, J = 8 Hz), 3.40 (2 H, s), 4.30 (2 H, br s).

Anal. Calcd for $C_5H_{12}O_2$: C, 57.66; H, 11.61. Found: C, 58.18; H, 11.70.

8b:[19] mp 45 °C (from petroleum ether, lit.[20] mp 46 °C); mass spectrum, m/e 101 (M – 17), 89, 87 (base peak), 71, 69, 58; IR ν_{max} 3360, 2950, 2920, 2870, 1455, 1135, 1065, 1045 cm^{-1}; NMR δ 0.82 (6 H, t, J = 8 Hz), 1.36 (4 H, q, J = 8 Hz), 3.23 (2 H, s), 3.84 (2 H, br s).

Anal. Calcd for $C_6H_{14}O_2$: C, 60.98; H, 11.94. Found: C, 61.57; H, 12.14.

8c:[19] mass spectrum, m/e 103 (M – 15), 101, 87, 75 (base peak), 69, 57; IR ν_{max} 3350, 2945, 2920, 2865, 1465, 1380, 1140, 1045 cm^{-1}; NMR δ 0.86 (3 H, m), 1.00 (3 H, s), 1.30 (4 H, m), 3.15 (2 H, s), 3.95 (2 H, br s).

Anal. Calcd for $C_6H_{14}O_2$: C, 60.98; H, 11.94. Found: C, 60.95; H, 12.03.

8d: IR ν_{max} 3360, 2945, 2860, 1050 cm^{-1}; NMR δ 1.4–2.0 (8 H m), 3.40 (2 H, s), 4.50 (2 H, br s).

8e: mp 72 °C (from petroleum ether, lit.[21] mp 68–70 °C); IR (KBr) ν_{max} 3300, 2920, 2840, 1445, 1040 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.7 (10 H, m), 2.40 (2 H, br), 3.42 (2 H, br s).

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.38; H, 10.97.

8f: mp 48 °C (from petroleum ether, lit.[22] mp 50–51 °C); IR ν_{max} 3370, 2915, 2850, 1460, 1070, 1025 cm^{-1}; NMR δ 1.2–1.9 (12 H, m), 3.26 (2 H, s), 3.96 (2 H, br).

***cis*- and *trans*-8g:** IR ν_{max} 3400, 2920, 2850, 1460, 1450, 1060, 1020, 990 cm^{-1}; NMR δ 0.85 (3 H, m), 1.0–1.85 (9 H, m), 3.23 and 3.56 (2 H, AB q, J = 11 Hz), 3.40 (2 H, br s).

***cis*- and *trans*-8h:** IR ($CHCl_3$) ν_{max} 3400, 2930, 1360, 1190, 1020 cm^{-1}; NMR ($CDCl_3$) δ 0.85 and 0.88 (9 H, 2 s), 1.0–2.0 (9 H, m), 2.20 (2 H, br), 3.43 and 3.60 (2 H, 2 s).

9e (stereoisomeric mixture): mass spectrum, m/e 210 (M, base peak), 181, 167, 112, 95; IR ν_{max} 2920, 2850, 1450, 1360, 1280, 1160, 1105, 1090, 1050, 940 cm^{-1}; NMR δ 1.2–1.8 (20 H, m), 3.60 (2 H, s).

9g (stereoisomeric mixture): IR ν_{max} 2925, 2855, 1460, 1450, 1380, 1180, 1160, 1140, 1100, 1060 cm^{-1}; NMR δ 0.90 (6 H, m), 1.10–1.95 (18 H, m), 3.45–3.82 (2 H, m).

9h (stereoisomeric mixture): mass spectrum, m/e 322 (M), 223, 151, 95 (base peak), 72; IR ν_{max} 2840, 1440, 1360, 1215, 1190, 1090, 1040 cm^{-1}; NMR δ 0.85 (18 H, s), 1.0–1.95 (18 H, m), 3.64, 3.68, 3.76, 3.78 (2 H, 4 s).

***cis*-10**: IR ($CHCl_3$) ν_{max} 3430, 2930, 2850, 1760, 1445, 1370, 1095, 990 cm^{-1}; NMR ($CDCl_3$) δ 1.1–2.0 (8 H, m), 2.15 (1 H, dd, J = 4, 12 Hz), 2.05 (1 H, s), 4.01 and 4.21 (2 H, AB q, J = 10 Hz).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.69; H, 8.07.

***trans*-10**: IR ($CHCl_3$) ν_{max} 3400, 2920, 2850, 1765, 1440, 1370, 1340, 1300, 1100, 1010, 900 cm^{-1}; NMR ($CDCl_3$) δ 1.2–2.1 (8 H, m), 2.50 (1 H, t, J = 6.3 Hz), 2.80 (1 H, br), 3.98 and 4.04 (2 H, AB q, J = 10 Hz).

11 (stereoisomeric mixture): IR (neat) ν_{max} 3430, 2930, 2855, 1703, 1440, 1365, 1190, 1150, 1045 cm^{-1}; NMR ($CDCl_3$) δ 1.0–2.0 (8 H, m), 2.40 (1 H, dd, J = 5, 11 Hz), 3.32 (2 H, s), 3.4 (1 H, br), 3.70 (3 H, s), 3.96 (1 H, br).

12: mass spectrum, m/e 152 (M), 109 (base peak), 81; IR ($CHCl_3$) ν_{max} 2930, 2860, 1735, 1440, 1420, 1320, 1030 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (3 H, d, J = 7 Hz), 1.71 (4 H, m), 2.21 (4 H, m), 4.80 (1 H, q, J = 7 Hz).

13: IR ($CHCl_3$) ν_{max} 3430, 2975, 2930, 2870, 1760, 1460, 1383, 1235, 1160, 1100, 1057, 945 cm^{-1}; NMR ($CDCl_3$) δ 1.31 (3 H, s), 1.7–2.65 (4 H, m), 3.46 and 3.54 (2 H, AB q, J = 11 Hz), 3.75 (1 H, br s).

14: IR ($CHCl_3$) ν_{max} 3590, 3450, 3000, 2975, 2900, 1775, 1470, 1410, 1385, 1265, 1110, 1025 cm^{-1}; NMR ($CDCl_3$) δ 1.46 (3 H, s), 2.56 (2 H, s), 3.70 (1 H, br), 4.09 and 4.22 (2 H, AB q, J = 10 Hz).

***p*-Toluenesulfonylation of 8g.** A stereoisomeric mixture of **8g**, obtained from 1.12 g of **7g**, and 1.15 g of *p*-toluenesulfonyl chloride was dissolved in 10 mL of pyridine, and the solution was stirred for 60 h at room temperature. The solution was neutralized with 2 M hydrochloric acid and extracted with dichloromethane. The residue, left after the solvent was removed in vacuo, was purified by preparative TLC, and *cis*- and *trans*-toluenesulfonate **15** were isolated.

***cis*-15:** IR (neat) ν_{max} 3530, 3050, 2920, 2850, 1595, 1445, 1350, 1175, 1100, 965, 840, 810 cm^{-1}; NMR ($CDCl_3$) δ 0.75 (3 H, d, J = 7 Hz), 1.1–1.7 (9 H, m), 1.75 (1 H, s), 2.40 (3 H, s), 3.81 (2 H, s), 7.22 (2 H, d, J = 10 Hz), 7.68 (2 H, d, J = 10 Hz).

***trans*-15:** IR (neat) ν_{max} 3520, 3050, 2920, 2850, 1595, 1445, 1355, 1175, 1100, 960, 835, 810 cm^{-1}; NMR ($CDCl_3$) δ 0.86 (3 H, d, J = 7 Hz), 1.1–1.9 (9 H, m), 2.15 (1 H, br), 2.42 (3 H, s), 3.93 (2 H, s), 7.28 (2 H, d, J = 10 Hz), 7.72 (2 H, d, J = 10 Hz).

Reduction of 15. A solution of *cis*-**15** (140 mg) and lithium aluminum hydride (40 mg) in tetrahydrofuran (10 mL) was refluxed for 3 h. The workup afforded *cis*-1,2-dimethylcyclohexanol.[4] By the same method, *trans*-1,2-dimethylcyclohexanol[4] was obtained from *trans*-**15**.

***p*-Toluenesulfonylation of 8h.** In the same way as described above, *cis*- and *trans*-**16** were isolated in pure state.

***cis*-16:** NMR ($CDCl_3$) δ 0.84 (9 H, s), 1.2–1.7 (9 H, m), 1.75 (1 H, br s), 2.47 (3 H, s), 3.85 (2 H, s), 7.45 (2 H, d, J = 10 Hz), 7.91 (2 H, d, J = 10 Hz).

***trans*-16:** NMR ($CDCl_3$) δ 0.79 (9 H, s), 1.2–2.0 (10 H, m), 2.47 (3 H, s), 4.05 (2 H, s), 7.48 (2 H, d, J = 10 Hz), 7.94 (2 H, d, J = 10 Hz).

Reduction of 16. In the same way as described above, each isomer of **16** was reduced with lithium aluminum hydride to the corresponding 4-*tert*-butyl-1-methylcyclohexanol.[5]

Frontalin. A solution of heptane-2,6-dione (**18**, 1.755 g) and $TiCl_4$ (0.75 mL) in CH_3OH (150 mL) was irradiated for 3 h. The clear blue solution was diluted with water and extracted with CH_2Cl_2. Evaporation of the solvent left almost pure frontalin as a colorless oil (76%). Slightly better yields (~85%) were obtained when irradiation was carried out in CH_3OH containing 20–30% CH_2Cl_2. Distillation gave pure frontalin: 1.136 g (58.3%); bp 90 °C (94 mmHg). The product had spectroscopic data (NMR, IR, and mass spectra) identical with those of (*S*)-(–)-frontalin.[9]

For a larger scale preparation, the following apparatus was used. A spiral, 55 mm in diameter and 100 mm in length, made of quartz tube (4 mm in diameter) was placed around the 1 kW high-pressure mercury lamp (Sen HL-1000 W (1 KW)), and the whole system was immersed in running water. The spiral part just fits the emitting portion of the lamp. The reactant solution was pumped into the spiral tube at a flow rate of 50 mL/60 min. This allows the solution to circulate the irradiated area in 20 min. By this method, any desired amount of the product can be prepared continuously without changing the reaction conditions.

Registry No. 7a, 78-93-3; **7b**, 96-22-0; **7c**, 107-87-9; **7d**, 120-92-3; **7e**, 108-94-1; **7f**, 502-42-1; **7g**, 583-60-8; **7h**, 98-53-3; **7i**, 1655-07-8; **7j**, 123-76-2; **7k**, 539-88-8; **8a**, 41051-72-3; **8b**, 66553-16-0; **8c**, 20667-05-4; **8d**, 74397-18-5; **8e**, 15753-47-6; **8f**, 74397-19-6; *cis*-**8g**, 74397-20-9; *trans*-**8g**, 74397-21-0; *cis*-**8h**, 60380-79-2; *trans*-**8h**, 60380-83-8; **9e**,

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178-99-4; **9g**, 74397-22-1; **9h**, 74397-23-2; *cis*-**10**, 74397-24-3; *trans*-**10**, 74397-25-4; *cis*-**11**, 74397-26-5; *trans*-**11**, 74397-27-6; **12**, 68965-57-1; **13**, 74397-28-7; **14**, 34945-05-6; *cis*-**15**, 74397-29-8; *trans*-**15**, 74397-30-1; *cis*-**16**, 74397-31-2; *trans*-**16**, 74397-32-3; **17**, 57917-95-0; **18**, 13505-34-5; *cis*-1,2-dimethylcyclohexanol, 19879-11-9; *trans*-1,2-dimethylcyclohexanol, 19879-12-0; *cis*-4-*tert*-butyl-1-methylcyclohexanol, 16980-56-6; *trans*-4-*tert*-butyl-1-methylcyclohexanol, 16980-55-5.

Photochemical Transformations of *cis*-1,2-Dibenzoylalkenes[1]

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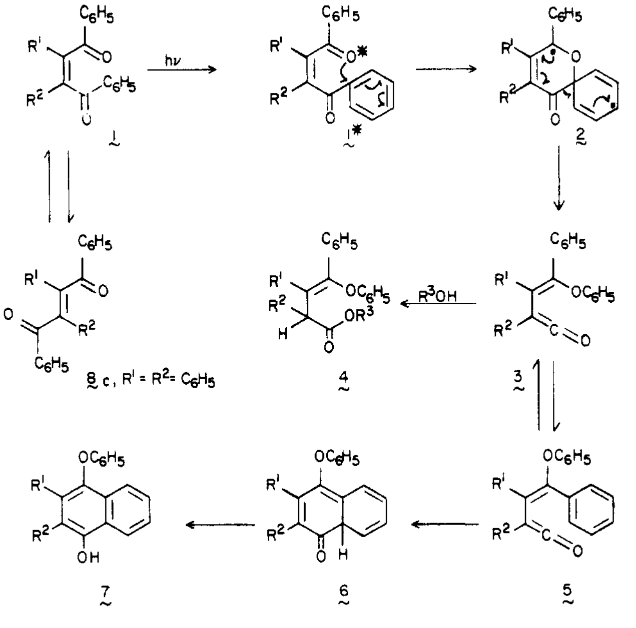
Photorearrangements of *cis*-1,2-dibenzoylalkenes such as 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**9**), 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (**21**), 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (**28**), and 2,3-dibenzoylbicyclo-[2.2.1]hepta-2,5-diene (**35**) are reported. Irradiation of **9** in methanol gives a mixture of isomeric esters **13** (69%) and **14** (1%), whereas in benzene a mixture of carboxylic acids **10** (26%) and **11** (6%) and lactone **12** (23%) is formed. Similar rearrangements have been observed in the case of **21** and **28**. Irradiation of **35** in benzene, however, gives mostly the quadricyclane **36**. Laser flash-photolysis studies have shown that diradical intermediates such as **18** and **19** may be involved in the transformation of **9** to the different products. Similar diradical intermediates have been postulated in the rearrangements of **21** and **28**.

Introduction

It has been shown by Griffin and O'Connell[3] and also by Zimmerman and co-workers[4,5] that dibenzoylethylenes (**1**) undergo an interesting photorearrangement in protic solvents, leading to the formation of the corresponding esters (**4**) (Scheme I). Thus, it has been observed that the photolysis of dibenzoylethylene (**1a**) in ethanol leads to the formation of 4-phenyl-4-phenoxy-3-butenoate (**4a**). Similar transformations have been observed in the case of both dibenzoylstyrene (**1b**) and dibenzoylstilbene (**1c**), leading to the formation of the corresponding esters **4b** and **4c**, respectively. In a recent investigation, Padwa et al.[6] have shown that the photolysis of *trans*-dibenzoylstilbene (**8c**) gives rise to different products, depending on the nature of the solvent employed. Thus, the photolysis of **8c** in benzene, for example, gives a mixture of products consisting of *cis*-dibenzoylstilbene (**1c**) and 1-hydroxy-2,3-diphenyl-4-phenoxynaphthalene (**7**), whereas 2,3,4-triphenyl-4-phenoxy-3-butenoic acid (**4d**) is formed in aqueous dioxane. Similarly, Sugiyama and Kashima[7] have observed that the photolysis of dibenzoylethylene (**1a**) in acidic methanol results in the formation of a mixture of products consisting of methyl 4-phenyl-4-phenoxy-3-butenoate, 1,2-dibenzoyl-1-methoxyethane, and 2,5-diphenylfuran. Also, it might be pointed out in this connection that tetrabenzoylethylene is reported to undergo photochemical transformation to an isomeric lactone.[8]

Scheme I



1a, $R^1 = R^2 = H$
1b, $R^1 = H$; $R^2 = C_6H_5$
1c, $R^1 = R^2 = C_6H_5$

4a, $R^1 = R^2 = H$; $R^3 = C_2H_5$
4b, $R^1 = H$; $R^2 = C_6H_5$; $R^3 = C_2H_5$
4c, $R^1 = R^2 = C_6H_5$; $R^3 = CH_3$
4d, $R^1 = R^2 = R^3 = H$

Zimmerman and co-workers[4,5] have suggested that the phototransformations of dibenzoylethylenes (**1**) to the corresponding esters (**4**) can be rationalized in terms of the pathway shown in Scheme I. On the basis of detailed quenching studies they have also suggested that the pho-

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