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Metal-catalyzed Organic Photoreactions. Photoreactions of Compounds Containing a Carbon-oxygen or Carbon-nitrogen Multiple Bond with Alcohols in the Presence of Titanium(IV) Chloride or Uranyl Chloride[1]

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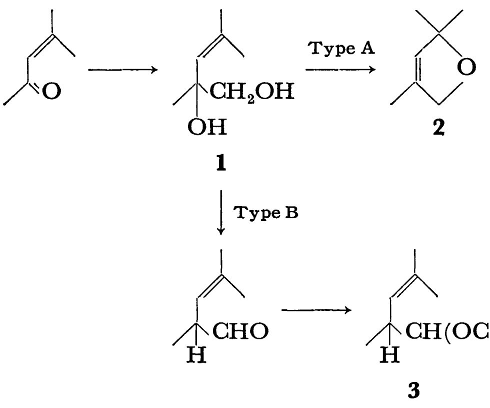
α,β-Unsaturated carbonyl compounds and esters, cyclopropyl ketones, β-diketones, Schiff's bases, and nitriles were irradiated in several alcohols in the presence of titanium(IV) chloride or uranyl chloride. In the titanium(IV) chloride-catalyzed reactions, the α-carbon atom of the primary alcohols underwent a bond formation, generally with the C=X (or C≡N) carbon atom of the substrates, while the bond formation occurred on a C=C carbon atom of the substrates in the uranyl chloride-catalyzed reactions. The reactions were examined under several conditions, and a possible scheme for the reactions was suggested.

We previously reported[2] that α,β-unsaturated ketones, when irradiated in alcohols in the presence of titanium(IV) chloride, underwent novel types of reaction with the formation of a C–C bond between the carbonyl carbon atom and the α-carbon atom of the alcohols. Pulegone and dypnone afforded dihydrofurans **2** (Type A), while mesityl oxide and 3-methyl-2-cyclohexenone afforded acetals **3** (Type B); these reactions are shown schematically in Scheme 1.



Scheme 1.

In the present study, we found that the reaction is applicable to other types of compounds and that uranyl chloride is also effective as a photocatalyst, but in a different mode from that observed with titanium(IV) chloride.

Results

Photoreactions in Methanol. α,β-Unsaturated carbonyl compounds and esters, cyclopropyl ketones, β-diketones, Schiff's bases, and nitriles were irradiated in methanol in the presence of titanium(IV) chloride or uranyl chloride. Several types of reactions were disclosed; the results are summarized in Tables 1 and 2. Evidently, in view of the observations obtained so far, the compounds containing a newly-formed C–C bond are products formed through the cooperation of light and the catalyst. The details concerning some blank experiments will be described in the Experimental part. The structure determinations of the products were done referring mostly to the spectroscopic data. Further support for the structures was also obtained from the following observations.

Photoreactions in the Presence of Titanium(IV) Chloride. α,β-Unsaturated Ketones: The irradiation of 1-acetylcyclopentene (**4**) gave glycol monomethyl ether **5**, acetal **6**, and methoxy ketone **7** (Run 1). The structure of **5** was supported by oxidizing it to an aldehyde **70**. Compound **5** corresponds to the diol **1**, which had been speculated as an intermediate for the formation of **2** or **3** (Scheme 1). Some reactions which terminated at the diol stage were also discovered in another systems (*vide infra*), and we classify these reactions as Type C. Several efforts to convert **5** into **6** were, however, unsuccessful.

Unlike the case of 3-methyl-2-cyclohexenone, which afforded an acetal *via* a Type B reaction,[2] 2-methyl-2-cyclohexenone (**8**) afforded a product in which two carbon units had been introduced (Run 2). The structure **9** was assigned to the product because it gave *o*-ethyltoluene upon treatment with hydrochloric acid through the elimination of water and methanol and a succeeding proton rearrangement. In order to eliminate the alternative structure **71**, which is also consistent with the observed spectroscopic data, we oxidized **9** with CrO_3–pyridine–HCl. Besides the main product **72** (the structure is not fully conclusive; see Experimental part), a small amount of a methoxy aldehyde **73** was isolated, which definitely supported the structure **9**. Further support for favoring **9** over **71** was obtained because the chemical shift of the *O*-methylene protons in **9** exhibited a greater down-field shift ($\Delta\delta \approx 0.6$ ppm) than that of the *O*-methine proton ($\Delta\delta \approx 0.1$ ppm) when derived into a phenylurethane derivative.

Reaction **8**→**9** can be shown schematically by the consecutive steps of: (1) the Type B reaction from **8** to form **74**: (2) the isomerization of **74** into an α,β-unsaturated aldehyde **75**, and (3) the Type C reaction from **75** to produce **9**. The photoreactions of α,β-unsaturated aldehydes will be described in the following section.

The absence of a methyl group in the 2-cyclohexenone system induced the reaction to proceed by way of a

TABLE 1. $TiCl_4$-CATALYZED PHOTOREACTIONS

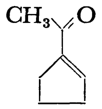
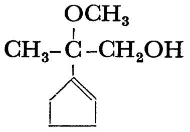
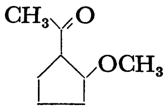
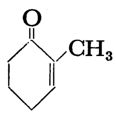
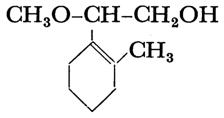
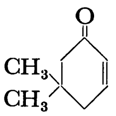
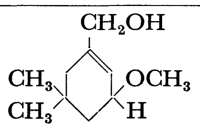
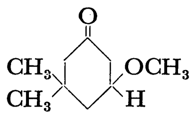
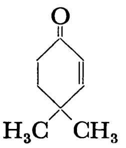
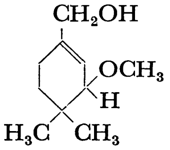
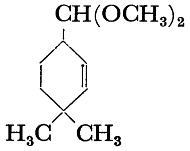
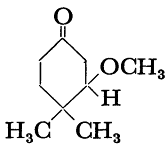
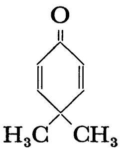
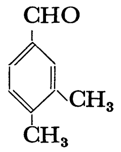
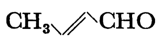
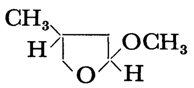
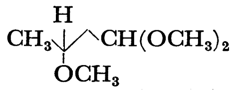
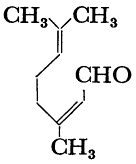
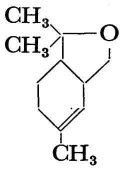
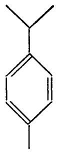
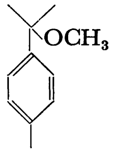
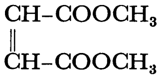
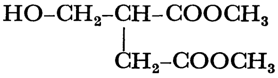
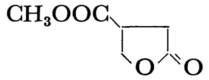
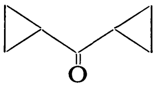
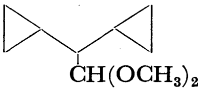
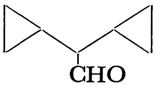
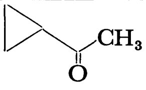
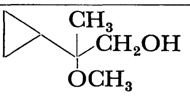
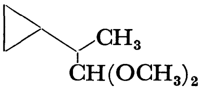
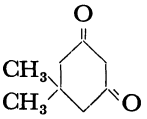
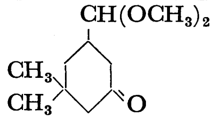
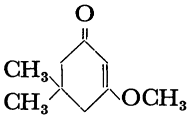
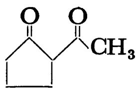
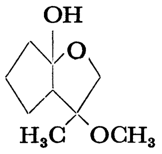
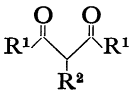
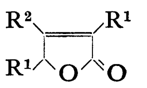
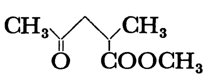
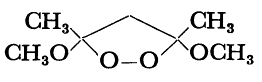
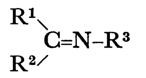
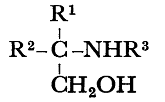
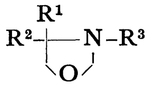
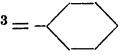
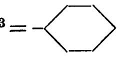
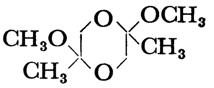
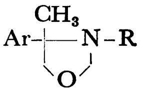
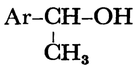
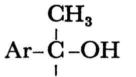
Runs	Starting materials	Products (yields, %)		
1	 **4**	 **5**(25)	 **6**(4)	 **7**(5)
2	 **8**	 **9**(32)		
3	 **10**	 **11**(45)	 **12**(trace)	
4	 **13**	 **14**(18)	 **15**(16)	 **16**(8)
5	 **17**	 **18**(32)		
6[a]	 **19**	 **20**(60)	 **21**(trace)	
7	 **22**	 **23**(18)	 **24**(4)	 **25**(4)
8	 $CH{-}COOCH_3 \atop {\parallel \atop CH{-}COOCH_3}$ **26**	 $HO{-}CH_2{-}\underset{\displaystyle CH_2{-}COOCH_3}{CH}{-}COOCH_3$ **27** (66:34)	 **28**	
9	 **29**	 **30**(95)	 **31**(trace)	
10	 **32**	 **33**(60)	 **34**(5)	
11	 **35**	 **36**(44—60)	 **37**(20—10)	

Table 1. (Continued)

Runs	Starting materials		Products (yields, %)		
12					
		38	**39** (60)		
					
13	$R^1=CH_3$ $R^2=H$	**40**	**41** (5)	**42** (18)	**43** (5)
14	$R^1=$Bu-*t* $R^2=H$	**44**	**45** (65)		
15	$R^1=R^2=CH_3$	**46**	**47** (n.d.)[b]		
			 $R^2\text{-}\overset{R^1}{\underset{CH_2OH}{C}}\text{-}NHR^3$		
16	$R^1=Ph$, $R^2=H$ $R^3=CH_3$	**48**	**49** (80)	**50** (20)	
17	$R^1=Ph$, $R^2=H$ $R^3=$- 	**51**	**52** (90)	**53** (trace)	
18	$R^1=n\text{-}C_5H_{11}$ $R^2=H$ $R^3=$- 	**54**	**55** (n.d.)	**56** (n.d.)	
19	$R^1=Ph$ $R^2=R^3=CH_3$	**57**	**58** (3:2)	**59**	
20	CH_3CN				
		60	**61** (8)		
	ArCN			 $Ar\text{-}\underset{CH_3}{CH}\text{-}OH$	 $Ar\text{-}\overset{CH_3}{\underset{CH_2OH}{C}}\text{-}OH$
21	Ar=Ph	**62**	$R=CH_3$ **59** (20)	**63** (trace)	**64** (trace)
22	Ar=*p*-Tol	**65**	R=H **66** (11)	**67** (trace)	
23	Ar=*o*-Tol	**68**	R=H **69** (15)		

a) $SnCl_4$-catalyzed reaction. b) Not determined.

Table 2. UO_2Cl_2-catalyzed photoreactions

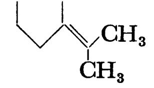
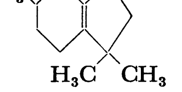
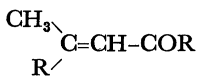
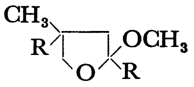
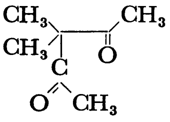
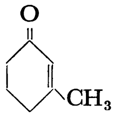
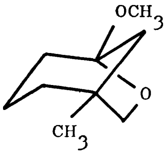
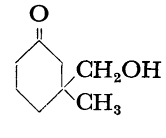
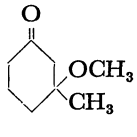
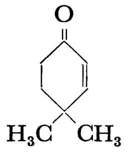
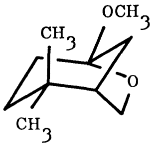
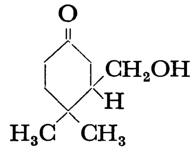
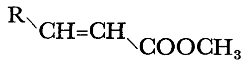
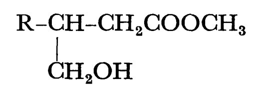
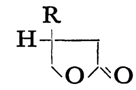
Runs	Starting materials		Products (yields, %)	
24				
		91	**92** (71)	
				
25	R=H	**19**	**20** (19)	
26	$R=CH_3$	**93**	**94** (45)	**95** (trace)

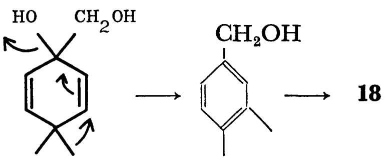
Table 2. (Continued)

Runs	Starting materials	Products (yields, %)		
27	 **96**	 **97** (17)	 **98** (0—2)	 **99** (15)
28	 **13**	 **100** (4)	 **101** (9)	
	 $R-CH=CH-COOCH_3$	 $R-CH(CH_2OH)-CH_2COOCH_3$		
29	$R=COOCH_3$ **26**	**27** (65)	**28** (6)	
30	$R=CH_3$ **102**	**103** (47)	**104** (11)	
31	R=H **105**	**106** (13)	**107** (1)	

different course. The irradiation of **10** afforded a methoxy alcohol **11** as a titanium(IV) chloride-catalyzed photoproduct (Run 3). The oxidation of **11** with CrO_3–pyridine–HCl afforded an aldehyde **77**. The formation of **11** can be considered to involve the Type C reaction to produce a diol **76** followed by an S_N' reaction by the methoxyl group.

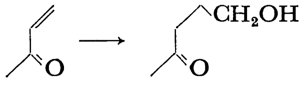
Since it is widely known that the photoreactions of cyclohexenone and cyclohexadienone systems proceed in a unique way to produce "lumi-products," we carried out the titanium(IV) chloride-catalyzed photoreactions with these substances. The products from **13** were methoxy alcohol **14**, acetal **15**, and a methoxy ketone **16** (Run 4). Evidently **14** and **15** are typical products *via* the titanium(IV) chloride-catalyzed photoreaction, and no products *via* "lumi products" were identified. The structure of **15** was confirmed by hydrolyzing it to an aldehyde **78**, and that of the alcohol **14**, by oxidizing it to an aldehyde **79**. The formation of **14** is another instance of a 2-cyclohexenone system carrying no methyl group.

The irradiation of **17** gave 3,4-dimethylbenzaldehyde (**18**) (Run 5). A possible sequence for the formation of this aromatic aldehyde is an initial hydroxymethylation (Type C), followed by aromatization, with a methyl migration and the succeeding oxidation of the benzyl alcohol to the aldehyde (Scheme 2). However, benzyl alcohol afforded benzyl methyl ether selectively without being oxidized to benzaldehyde under the same reaction conditions.



Scheme 2.

α,β-Unsaturated Aldehydes: With a view to comparing the reactivities of ketones and aldehydes, 2-butenal (crotonaldehyde, **19**) and 3,7-dimethyl-2,6-octadienal (citral, **22**) were irradiated under the same conditions. In contrast with the ketone system, **19** afforded a cyclic acetal **20** as the titanium(IV) chloride-catalyzed photoproduct (Run 6). The acetal was isolated as a mixture of *cis*- and *trans*-isomers, which could not be separated by GLC. The NMR spectrum was obtained as a sum of the two spectra, but on adding $Eu(DPM)_3$, each signal separated sufficiently well for the assignment to be made. We assumed that the methyl signal in the *cis*-isomer would exhibit a greater down-field shift when affected by the shift reagent as compared with that in the *trans*-isomer, and estimated the composition of *cis* to *trans* as 42: 58 from the intensities of the methyl signals of the two isomers.



Scheme 3.

It should be noted that the same reaction pattern was observed in the photoreaction under the catalytic action of tin(IV) chloride in place of titanium(IV) chloride. Generally, tin(IV) chloride did not reveal any catalytic activities in reaction to ketones. The formation of a by-product **21** was much less when tin(IV) chloride was used as the catalyst. The present reaction can be schematized as a 1,4-addition, in contrast with the 1,2-additions observed so far (Types A—C), and we would like to classify the reaction as Type D (Scheme 3). It was found that the 1,4-type reaction became the sole reaction pattern, even in a ketone system, when uranyl chloride was used as the catalyst (*vide infra*).

Type D is not necessarily an exclusive reaction type of unsaturated aldehydes. Citral (**22**), when allowed to react under the present reaction conditions, afforded a tetrahydrofuran **23**, along with **24** and **25** resulted from the titanium(IV) chloride-catalyzed dark reaction (Run 7). Evidently the reaction proceeded through the 1,2-type (Type C) to give **80**, followed by a cyclization involving a remote double bond.

α,β-Unsaturated Esters: It was found that the reaction of dimethyl maleate (**26**) was of the 1,4-type and afforded a hydroxymethyl derivative **27** and a lactone **28** (Run 8). Although the sensitized photoadditions of alcohols to α,β-unsaturated esters have been known to produce γ-butyrolactones,[3] the present reaction is considered to proceed through a different mechanism (see Discussion part). The hydroxymethyl derivative cyclized to the corresponding lactone upon heating at 150 °C and it can be assumed to be an intermediate to lactone. The same reaction occurred in the uranyl chloride-catalyzed photoreaction (*vide infra*).

Cyclopropyl Ketones: We observed that saturated alicyclic ketones (cyclohexanone and cycloheptanone) were intact under the present reaction conditions, and we were tempted to see if the cyclopropyl group would activate the carbonyl group to be involved in the present reaction. It was found that the two cyclopropyl ketones **29** and **32** mainly underwent Type B and Type C reactions to produce **30** (Run 9) and **33** (Run 10) respectively. The structure **30** was confirmed by comparing it with the sample prepared from the authentic aldehyde **31**. The structure of **33** was supported because the *O*-methylene protons exhibited an extensive down-field shift ($\Delta\delta \approx 0.6$ ppm) when the alcohol was derived into a phenylurethane derivative (*cf.* Run 2). Upon oxidation with CrO_3–pyridine–HCl, **33** gave an aldehyde **81**. When the work-up was performed after the irradiated solution had been refluxed, the acetal **34** became the sole product. This observation verifies the intermediacy of the diol **1** in the Type B reaction.

β-Diketones: 5,5-Dimethyl-1,3-cyclohexanedione (dimedone, **35**) afforded an acetal **36** and an enol ether **37**, upon the titanium(IV) chloride-catalyzed photoreaction (Run 11). Since the enol ether **37**, which is the exclusive product in the dark reaction of the present system, produced **36** under the same irradiation conditions, the reaction from **35** can be schemed as involving a primary dark step to produce **37**, followed by a Type B reaction to produce **36**. The acetal **36** gave an aldehyde **82** upon hydrolysis with hydrochloric acid.

Although 2-acetylcyclohexanone, under the present reaction conditions, afforded a complicated mixture of products, 2-acetylcyclopentanone (**38**) underwent a clear reaction (Run 12). The extraction of the reaction mixture and the evaporation of the solvent from the extract left an almost pure oil. The structure **39** is tentatively assigned as the product, although we could not eliminate the alternative structures such as **83** and **84**.

Unlike the cases of cyclic β-diketones mentioned above, open-chain β-diketones gave different types of products. Acetylacetone (**40**) afforded butenolide **41**, γ-keto ester **42**, and cyclic peroxide **43** (Run 13). The spectroscopic data of the butenolide **41** coincided with the reported data.[4] The structure of **42** was confirmed by comparing it with the authentic sample prepared from nitroethane and methyl methacrylate.[5] Evidently the oxidation state of the newly-introduced function is higher than those observed so far; we speculate a Cannizzaro-type oxidation of the intermediate aldehyde with the co-operation of the suitably located hydroxyl group and titanium to give the butenolide (*cf.* **86**), which partly undergoes methanolysis to afford a γ-keto ester **42**.

The formation of the cyclic peroxide **43** is without precedent, but it was found that its formation is not characteristic of the titanium(IV) chloride-catalyzed photoreaction. The peroxide was also obtained as the sole product by the hydrochloric acid-catalyzed photoreaction of **40**, although the rate in this case was much slower than the titanium(IV) chloride-catalyzed photoreaction.

The cyclic peroxide **43** was distillable under reduced pressure, but it decomposed cleanly into methyl acetate and methyl propionate at 150 °C (*cf.* **87**). When it was ignited, however, it was detonated violently. Its formation may be shown schematically as a proton-assisted addition of methanol to produce **88**, which was photooxidized to the product, titanium or oxygen in the air presumably serving as the oxidizing agent.

The reaction of 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane, **44**) was much more selective: the extraction of the irradiated solution with chloroform and the evaporation of the extract left a butenolide **45** as almost pure crystals in 65% yield (Run 14). The physical data of **45** and those of a reduction product **89** coincided with the reported values.[4]

In the same way, diketone **46** afforded a butenolide **47** under the same conditions (Run 15).

Schiff's Bases: In contrast with the diversity of the photoreactions reported with carbonyl compounds, only a few photoreactions of Schiff's bases have been known. However, it was found in the present study that the reactions of Schiff's bases also proceeded in a reaction pattern similar to that of carbonyl compounds when irradiated in the presence of titanium(IV) chloride.

The photoreaction of **48** afforded an oil which consisted of **49** as the main fraction, contaminated with a minor amount of **50**, as revealed by the NMR analysis (Run 16). No appreciable intensities of signals assignable to the other compounds were observed. Although **49** was stable in the presence of titanium(IV) chloride, it decomposed (probably polymerized) completely after 24 h at room temperature when isolated free from titanium(IV) chloride. From this mixture, a pure sample of **50** was isolated by column chromatography. The structure of **49** was confirmed by deriving it to the bis(*p*-nitrobenzoyl) derivative and the picrate. The formation of **49** is reasonable in view of the Type C reaction observed with carbonyl compounds. The oxazolidine **50** must be a secondary product from **49** and formaldehyde, which had been photolytically produced from methanol and titanium(IV) chloride. Actually, **49** was quantitatively transformed into **50** upon treatment with formalin.

An example of the formation of oxazolidine upon the irradiation of Schiff's base in methanol has been reported by Cerutti and Schmid.⁶⁾ In the present case, however, it was confirmed that **49** and **50** were obtained only with the cooperation of light and titanium(IV) chloride. The same authors⁷⁾ reported the formation of imidazolidines **90** (*dl* and *meso*) from **48** through photoreductive dimerization, followed by the condensation of formaldehyde. These products were not identified under the present reaction conditions. The formation of the imidazolidines became the main reaction path upon irradiation in the presence of titanium(IV) chloride and sodium methoxide, which will be described in the next section.

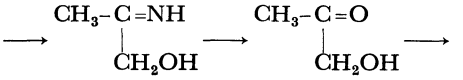
A selective photoreaction was also observed in the case of **51** (Run 17). The extraction of the reaction mixture with chloroform and the evaporation of the extract left crystals of **52** in an almost pure state in a high yield. The treatment of **52** with formalin again afforded an oxazolidine **53**. Similarly, **54** afforded **55** and **56** under the same conditions (Run 18).

The photoreaction of ketimine also proceeded in the same way (Run 19). The NMR analysis of the crude reaction mixture from **57** revealed that the products are mainly **58**, accompanied by a small amount of **59**. The treatment of the crude mixture with formalin afforded **59**.

Nitriles: It has been established that the photochemical reaction of aromatic and aliphatic nitriles proceeds mostly on the carbon-carbon double bond (even in an aromatic system), to the exclusion of any products from the reaction at the cyano group. To the best of our knowledge, exceptions have been reported only by Cantrell⁸⁾ and recently by Yang,⁹⁾ who observed a 2+2 cycloaddition at the nitrile function upon the irradiation of aromatic nitriles with certain electron-rich olefins.

We have now observed that the cyano group was also induced to be involved in the photoreaction in the presence of titanium(IV) chloride. The irradiation of acetonitrile (**60**) gave a mixture of two stereoisomers (3: 1) of **61** as the exclusive non-volatile product. Recrystallization furnished the major component as a pure sample which was identical with the crystals separated out from a 50% methanol solution of hydroxyacetone, but the stereochemistry was not elucidated. The reaction can be shown schematically as similar to a Type C reaction, followed by hydrolysis and dimerization (Scheme 4).

60



$$\mathbf{60} \longrightarrow \underset{\mathrm{CH_2OH}}{\mathrm{CH_3{-}\overset{}{C}{=}NH}} \longrightarrow \underset{\mathrm{CH_2OH}}{\mathrm{CH_3{-}C{=}O}} \longrightarrow \mathbf{61}$$

61

Scheme 4.

In contrast with the simple reaction observed with acetonitrile, the photoreaction of aromatic nitriles gave products exceeding expectations. The major product from benzonitrile (**62**) was a *C*- and *N*-methylated oxazolidine **59** (Run 21), which was identical with the product obtained from *N*-(α-methylbenzylidene)methylamine in Run 19. Similar reactions were observed with *p*- and *o*-tolunitrile, although no *N*-methylation was observed with the tolunitrile system (Runs 22 and 23). The by-product **63** was identified by comparison with an authentic sample. The by-product **64** was identical with the sample obtained in a small amount by the irradiation of acetophenone in methanol in the presence of titanium(IV) chloride.

No reasonable scheme for the *C*- and *N*-methylation can be proposed. For the titanium(IV) chloride-catalyzed photoreactions of ketones, we previously proposed a mechanism involving primary electron transfer from methanol to the carbonyl compound, followed by the proton transfer and cross-coupling of the resulting radicals.²⁾ In compliance with this scheme, we postulated in our previous communication¹ᵇ⁾ a mechanism involving phenylazirine as a possible intermediate for the reaction. The scheme seemed to be attractive, but it has now been found to be unfavorable since phenylazirine did not afford the oxazolidine **59** under the present reaction conditions. Although the structure of the actual product, which was obtained as crystals, has not been determined, the NMR analysis indicated that neither *C*-methylation nor *N*-methylation took place on phenylazirine.

Photoreactions in the Presence of Uranyl Chloride. In contrast with the 1,2-type reactions (Types A—C) observed with most of the α,β-unsaturated carbonyl compounds (except in the cases of Runs 6 and 8), the photoreactions in the presence of uranyl chloride were of the 1,4-type (Type D, Scheme 3). The results are summarized in Table 2.

The primary products from **91** seem to be a mixture of stereoisomers of **108**, as revealed by NMR analysis, but these compounds decomposed cleanly into **92** upon vacuum distillation (Run 24).

The reaction of 2-butenal (**19**) proceeded in the same way (including stereochemistry) as the titanium(IV) chloride- and tin(IV) chloride-catalyzed reactions (Run 25, *cf.* Run 6). Similarly, mesityl oxide (**93**) furnished **94** as the main product, accompanied by a trace amount of **95** (Run 26). Small amount of **95** was also identified in the reactions in other alcohols (ethanol, 1- and 2-propanol, and water–2-methyl-2-propanol (1: 1), *vide infra*); it is speculated that this product arose through the addition of the acetyl radical, which had been formed from **93** in a certain stage of the reaction, to another molecule of **93**. The addition of the acetyl radical to **93** to produce **95** has been reported.¹⁰⁾ The hydrolysis of **94** with hydrochloric acid gave a product which could be identified by NMR analysis as a tautomeric mixture of **109a** and **110a** (1: 1).¹¹⁾ The mixture, upon oxidation with CrO_3–pyridine–HCl, afforded a keto aldehyde **111** as the sole product.

The reaction of **96** produced **97** as the main product, accompanied by a small amount of a methanol adduct **99** (Run 27). A vacuum distillation of the mixture induced the elimination of methanol from **99**; the distillate consisted of **97** and the starting ketone **96**. The yields of products in the uranyl chloride-catalyzed reactions are sensitive to the reaction conditions (light intensities, duration of irradiation, quality of the catalyst, and pH of the solution; *vide infra*), and the ring-opened product **98** was identified, along with the major product **97**, on some reactions of **96**.

The enone **13** also gave a ring-opened alcohol **101**, as well as a cyclic acetal **100** (Run 28). The reaction path through the "lumi-products" was not observed in the present case either (*cf.* Run 4). The primary alcohols **98** and **101** were oxidized to the aldehydes **112** and **113** respectively.

The same type of reaction as observed with titanium(IV) chloride-catalyzed reaction proceeded with the esters **26**, **102**, and **105** (Runs 29—31). The yields in Run 31 are low because of the extensive polymerization of the starting material. The oxidation of the γ-hydroxy ester **106** with CrO$_3$–pyridine–HCl gave an aldehydic ester **114**. As has been observed in Run 8, **103** and **106** cyclized to lactones **104** and **107** respectively upon heating. It should be noted that, while shorter-wavelength light (quartz-filtered light) was necessary to induce the reaction in the titanium(IV) chloride-catalyzed reaction, Pyrex-filtered light induced the reaction well with catalytic assistance by uranyl chloride.

Table 3. Concentration effect of TiCl$_4$ upon the product yields in the reaction of **96**

TiCl$_4$ Mol equiv to **96**	**96** (Recovd) (%)	**115** (%)	**116a** (%)	**117a** (%)	**99** (%)
0.1	12	30	trace	trace	25
0.2	29	49	trace	trace	5
0.5	7	65	trace	trace	6
1.0	0	71	5	3	11
2.0	trace	70	5	2	trace
3.0	4	51	6	3	4
4.0	4	46	8	5	4
5.0	2	30	11	5	trace
10	trace	15	17	2	trace

Solutions of **96** (0.1 g, 0.91 mmol) and varying amounts of TiCl$_4$ in methanol (10 ml) were irradiated with Pyrex-filtered light for 7 h. The yields were determined by NMR analysis, using nitrobenzene as the internal reference.

Effects of the Reaction Conditions. Titanium(IV) Chloride-catalyzed Reactions: The effect of the catalyst concentration on the product yields was examined using 3-methyl-2-cyclohexenone (**96**) as the substrate. The yields of the products, as determined by NMR analysis, are summarized in Table 3. Although the maximum yield of the Type B products (**115**, **116a**, and **117a**) was obtained when about an equimolar amount of titanium(IV) chloride was used, it is evident that titanium(IV) chloride functions catalytically rather than stoichiometrically, because the amounts of the products exceed the amount of the catalyst at low concentrations of titanium(IV) chloride. Excess amounts of the catalyst complicated the reaction and afforded large amounts of by-products. At low concentration of titanium(IV) chloride, the polar addition of methanol to give **99** became efficient. Presumably the addition of methanol is catalyzed by the proton formed by the reaction of titanium(IV) chloride with methanol. It was confirmed that the proton-catalyzed photoaddition of methanol to **96** was remarkable at low concentrations of hydrochloric acid. Probably at higher proton concentrations, the thermal reverse reaction (elimination of methanol from **99**) would become efficient.

The reaction medium in the present reaction was acidic as a result of the formation of hydrochloric acid from titanium(IV) chloride and methanol. Since we observed, in our preliminary experiments,[2] that the acidic conditions are necessary to induce the present photoreaction, we carried out the titanium(IV) chloride-catalyzed photoreaction of **96** and **48** while adding varying amounts of sodium methoxide. Evidently the Type B reaction (**96**→**115**+**116a**+**117a**, Table 4) was retarded remarkably when the amount of sodium methoxide exceeded two mole equivalents of that of titanium(IV) chloride. The effect of the sodium methoxide concentration was also observed in the case of the photoreaction **48**→**49**+**50** (Run 16), as is shown in Table 5. Notably, there was a change in the reaction pattern, and imidazolidines **90** (*dl* and *meso*) became the products at higher concentrations of sodium methoxide. Cerutti and Schmid reported the formation of **90** by the irradiation of **48** in methanol with a low-pressure mercury lamp under argon.[7] Although we could not duplicate their results, the spectroscopic data on our

Table 4. Concentration effect of NaOCH$_3$ upon the product yields in the reaction of **96**

NaOCH$_3$ Mol equiv to TiCl$_4$	**96** (Recovd) (%)	**115** (%)	**116a** (%)	**117a** (%)	**99** (%)
0.5	trace	72	4	3	0
1.0	trace	63	5	2	0
1.5	0	65	4	2	0
2.0	61	6	trace	0	6
3.0	73	0	0	0	trace
4.0	55	0	0	0	trace

Solutions of **96** (0.1 g, 0.91 mmol), TiCl$_4$ (0.17 g, 0.91 mmol), and varying amounts of NaOCH$_3$ in methanol (10 ml) were irradiated and treated in the way described in the footnote in Table 3.

Table 5. Concentration effect of NaOCH$_3$ upon the product yield in the reaction of **48**

NaOCH$_3$ Mol equiv to TiCl$_4$	**50** (%)	*meso*-**90** (%)	*dl*-**90** (%)
0.0	71	0	0
1.0	67	0	0
2.0	66	0	0
3.0	50	0	0
4.0	19	7	6
5.0	5	15	13

Solutions of **48** (0.3 g, 2.5 mmol), TiCl$_4$ (0.17 g, 0.91 mmol), and varying amounts of NaOCH$_3$ in methanol (10 ml) were irradiated with quartz-filtered light for 3 h. An appropriate amount of 37% formalin was then added to the photolysate and the solution was worked-up in the way described in Run 16. The yields were determined by NMR analysis, using 1,1,2,2-tetrachloroethane as internal reference.

imidazolidines coincided with those previously reported.[12] *meso*-Imidazolidine **90** was prepared by the condensation of formaldehyde with an authentic ethylenediamine derivative **118** of mp 137 °C.[13] *dl*-Imidazolidine was also prepared from another isomer of **118**, which remained as an oil after the separation of the crystaline form of **118**.

We found that the imidazolidines were the sole products in the titanocene dichloride-catalyzed photoreaction of **48** in methanol. A decrease in the proton concentration or a change in the nature of the catalyst might be responsible for the effect of sodium methoxide, but no experimental evidence has been obtained.

Uranyl Ion-catalyzed Reactions: The uranyl chloride-catalyzed reaction is very sensitive to the pH of the solution. It was found from the experiment with **96** that the C–C bond-formation reaction proceeded most efficiently at pH 2—3. At pH 7, most of the starting material was recovered, while at pH 1, methanol addition to give **99** became the main reaction pattern.

The effect of the catalyst concentration on the product yields was examined using dimethyl maleate (**26**) as the substrate. In contrast with the case of the titanium(IV) chloride catalyst, the product yield (**27**+**28**) reached its maximum at a catalyst concentration of a one-tenth mole equivalent to that of the substrate, and thereafter held constant with increasing amounts of the catalyst. With increasing amounts of the catalyst, however, the cyclization to lactone (probably through the secondary thermal reaction) became appreciable.

Table 6. Effects of the counter ions in UO_2X_2 upon the product yields in the reaction (**26**→**27**+**28**)

Counter ions (X)	**26** (Recovd) (%)	**27**+**28** (%)
Cl	0	59
NO_3	52	24
OAc	79	8
SO_4	62	6

Solutions of **26** (0.15 g, 1.3 mmol) and uranyl compounds (0.13 mmol) in methanol (12 ml) was irradiated with Pyrex-filtered light for 6 h. The yields were determined by NMR analyses, using benzene as the internal reference. The yields of **28** did not exceed 3% of those of **27**.

It was found that the nature of the counter ions exerts a remarkable influence on the reaction of **26**, as is shown in Table 6. However, the trend should not be considered to be general, because uranyl sulfate was found to be as effective as uranyl chloride in the case of the reaction of mesityl oxide, although the acetate was poor in catalytic activity in both cases.

Reactions in the Other Solvents. Titanium(IV) Chloride-catalyzed Reaction of 3-Methyl-2-cyclohexenone (69): We have previously reported that the reaction of **96** in ethanol proceeded in the same way as in methanol to produce two methyl ketones **116b** (49%) and **117b** (12%).[2] The same type of reaction also occurred in other primary alcohols; the products were **116c** (34%) and **117c** (9%) in 1-propanol; **116d** (30%) and **117d** (8%) in 1-butanol; and **116e** (39%) in 2-methyl-1-propanol. Contrary to the primary alcohols, 2-propanol was found to be unreactive, the major part of the starting material being recovered unreacted, accompanied by a small amount of *m*-cymene (**119**), which is a product of a Type C reaction followed by dehydration and proton rearrangement. The reduced reactivity of 2-propanol was also indicated by the reaction of **96** in a mixed solvent of 2-propanol and methanol (1:1 by volume), which afforded a methanol-participated product **115** as the sole product. Most of the starting material was recovered by photoreactions in 2-butanol and 2-methyl-2-propanol.

Uranyl Chloride-catalyzed Reaction of Mesityl Oxide (93): The photoreaction of **93** in ethanol in the presence of uranyl chloride proceeded according to the same pattern as that in methanol and afforded a product which was identified by NMR analysis as a mixture of **109b** and **110b**. The subsequent oxidation of the product mixture by CrO_3–pyridine–HCl afforded **95** as the main product (13% from **93**), along with a small amount of a lactone **120**. The lactone must be a product of the oxidative demethylation from **110b**. In parallel with the observation described above, 2-propanol was also lacking the reactivity, and the products in this solvent were a diketone **95** and a cyclobutanol **121**. The diketone **95** became the major product by Pyrex-filtered light, while the ratio was reversed by quartz-filtered light. Both compounds were also the main products in a hydrochloric acid-catalyzed photoreaction in 2-propanol and in a titanium(IV) chloride-catalyzed photoreaction in water–2-methyl-2-propanol (1:1 by volume). The cyclobutanol **121** is known to be a photoproduct from 4-methylpent-4-en-2-one (isomesityl oxide),[14] and it can be presumed that the weak acidic conditions (pH 3) of the present reaction might catalyze the thermal isomerization of **93** into isomesityl oxide, from which the cyclobutanol is derived.

Uranyl Chloride-catalyzed Reactions of α,β-Unsaturated Esters: The reaction of dimethyl maleate (**26**) in ethanol proceeded in the same way as in methanol and furnished a mixture of *threo*-**122a**[15] (23%), *erythro*-**122a** (14%), *cis*-**123a** (13%), and *trans*-**123a** (6%), as revealed by NMR analysis. Heating induced cyclization, and a mixture of *cis*- and *trans*-**123a** was obtained. The assignments of the stereochemistry of the lactones were performed by referring to the reported data.[3b] The stereochemistry of the hydroxy esters **122a** was speculated from the relative amounts prior to and after the thermal cyclization to the lactones (*cf.* Experimental part).

In contrast with the reactions described above, 2-propanol was brought into the reaction with **26** with the catalytic assistance by uranyl chloride; we thus obtained **122b**, which was then further cyclized to a lactone **123b**.

Discussion

All the reactions described thus far can be shown schematically as involving a primary step of the formal addition of the hydroxymethyl radical to C=O, C=N, and C≡N groups (1,2-type, in the titanium(IV) chloride-catalyzed reactions) or to an unsaturated carbon atom (1,4-type, in the uranyl chloride-catalyzed reactions). The photochemical 1,4-additions of alcohols[16] or ethers[17] to α,β-unsaturated carbonyl compounds by means of aromatic-ketone sensitization have been reported with various systems, and have been shown schematically involving radical species. It seemed conceivable that the present reaction might proceed through a radical initiation, particularly when uranyl chloride was used as the catalyst, since such a catalyst might produce chlorine radicals upon irradiation. This hypothesis was examined and rejected on the basis of the following observations.

No traces of products characteristic of the present metal-catalyzed photoreactions were identified from mesityl oxide upon (1) refluxing in methanol for 50 h while benzoyl peroxide was being added, (2) irradiating in methanol in the presence of benzophenone, or (3) the bubbling of chlorine into the methanol solution under irradiation with a tungsten lamp. The reaction with chlorine gave **124** and one more compound whose structure has not been elucidated. The fact that uranyl sulfate is as effective as uranyl chloride would also eliminate the possible intervention of the chlorine radicals.

Table 7. Solvent effects upon the product yields in the reaction (**125**→**126**+**127**)

Alcohols	UO_2Cl_2-catalyzed				Benzophenone-sensitized	
	1 h		6 h		6 h	
	126 (%)	**127** (%)	**126** (%)	**127** (%)	**126** (%)	**127** (%)
Methanol	45	0	65	0	0.6	0
Ethanol	19	0	39	0	0.6	0
2-Propanol	0	7	5	24	1.0	1.3

A solution of **125** (0.15 g, 1.5 mmol) and UO_2Cl_2 (0.044 g, 0.13 mmol) or benzophenone (0.029 g, 0.16 mmol) in alcohol (12 ml) was irradiated with Pyrex-filtered light.

Although the benzophenone-sensitized additions of alcohols to ethyl 2-butenoate (**125**) have been reported to be effected under irradiation for 50—72 h,[3a)] no appreciable photoaddition was observed during the present irradiation time (1—6 h, see Table 7). The same authors investigated the photochemical addition of hydroxyalkyl groups to **125** with various alcohol systems, and found that the reactivities increased in the order of: methanol<ethanol<2-propanol, an order which is consistent with the proposed radical-chain mechanism. The same reactions with the catalytic assistance by uranyl chloride were now examined, and it was found that the order of the reactivities of these alcohols is completely reversed (Table 7). The decrease in the reactivities of the secondary alcohols, as observed in the cases described here and in the previous section, could be another evidence against the intervention of the free-radical species.

The uranyl ion-catalyzed photoisomerization of stilbene[18] and the photodimerization of dienone[19] have been reported. Energy transfer and a restricted orientation of dienone by coordination, respectively, have been presented as the mechanisms.

Table 8. Experimental conditions

Runs	Starting materials (g)	$TiCl_4$[a)] or UO_2Cl_2 (g)	Methanol (ml)	Tubes[c)]	Time (h)
1	**4**(0.3)	0.52	30	P	3
2	**8**(0.45)	0.78	45	P	6
3	**10**(0.10)	0.17	10	Q	5
4	**13**(1.40)	2.42	140	Q	4
5	**17**(0.04)	0.10	10	P	4
6	**19**(0.30)	0.52[d)]	36	Q	3
7	**22**(1.40)	2.42	140	Q	3
8	**26**(0.15)	0.26	12	Q	6
9	**29**(0.1)	0.17	13	Q	4
10	**32**(0.1)	0.17	13	Q	4
11	**35**(0.8)	1.4	80	P	5
12	**38**(0.6)	1.04	60	Q	6
13	**40**(1.6)	2.8	80	Q	7
14	**44**(0.4)	0.7	40	P	6
15	**46**(0.1)	0.17	10	Q	6
16	**48**(1.0)	2.1	120	Q	4
17	**51**(0.47)	0.8	56	Q	4
18	**54**(0.5)	1.04	60	Q	4
19	**57**(0.28)	0.7	48	Q	24
20	**60**(1.3)	1.4	80	Q	24
21	**62**(0.38)	0.66	48	Q	24
22	**65**(0.38)	0.66	48	Q	24
23	**68**(0.38)	0.66	48	Q	24
24	**91**(0.6)	0.24	72	P	5
25	**19**(0.8)	0.21	96	P	5
26	**93**(0.8)	0.2	96	P	5
27	**96**(0.8)	0.2	96	P	5
28	**13**(1.0)	0.15	80	P	7
29	**26**(1.0)	0.24	80	P	3
30	**102**(1.5)	0.51	120	P	6
31	**105**(1.5)	0.3	120	P	1

a) Runs 1—23. b) Runs 24—31. c) P: Pyrex, Q: quartz. d) $SnCl_4$.

The photoreaction of mesityl oxide in tetrahydrofuran in the presence of uranyl chloride resulted in the formation of a C–C bond, giving **128** as the main product (17%). The same product was obtained by the benzophenone-sensitized photoreaction, while the direct irradiation (without any additives) under the same conditions resulted in a recovery of the starting material, with a negligible formation of **128**. Evidently uranyl chloride functions as a sensitizer in the reaction in tetrahydrofuran, and the reaction proceeds through an intermediacy of the radical species, in marked contrast with the photoreactions in alcohols.

Some of the titanium(IV) chloride-catalyzed photoreactions were wave-length-dependent. Pyrex-filtered light could not induce the present reaction in the cases of 2-acetylcyclopentanone (**38**), dimethyl maleate (**26**), and acetonitrile (**60**). The acetylcyclopentanone **38** afforded **129**, while **26** and **60** were recovered intact under these conditions.

In considering possible mechanisms for the metal-

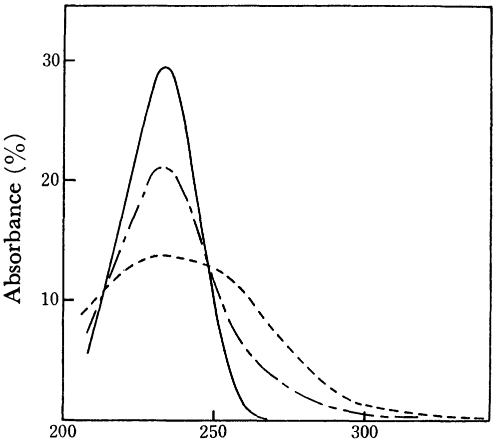


Fig. 1. Absorption spectra of **96** (——, 1.97×10^{-5} M, $\varepsilon=14900$), $TiCl_4$ (----, 1.96×10^{-5} M, $\varepsilon=6580$), and a mixture of an equal volume of both solutions (-----).

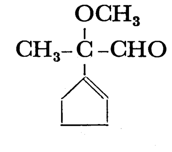
catalyzed photoreactions, it seems important to investigate the absorption characteristics. At low concentrations ($\approx 2\times10^{-5}$ M), the mixing of 3-methyl-2-cyclohexenone (**96**) and titanium(IV) chloride did not result in any changes in the absorption curves in the 220—320 nm region; only a sum of the two absorption curves was obtained (Fig. 1). The same phenomena were observed with the uranyl chloride–dimethyl maleate (**26**) and uranyl chloride–mesityl oxide (**93**) systems. It was revealed from the experiments with more concentrated solutions (concentrations corresponding to the actual reactions, 10^{-2}—10^{-1} M), however, that a new absorption band appeared in the 350—480 nm region upon the mixing of the substrate and the metal compound in the **96**–$TiCl_4$, **93**–$TiCl_4$, and **93**–UO_2Cl_2 systems, while no development of the new band was observable in the **26**–UO_2Cl_2, **26**–$TiCl_4$, and **60**–$TiCl_4$ systems. The absorption coefficients (ε) calculated by assuming the formation of a 1 : 1 complex between the substrate and the metal compound were 5—7. We have not identified the character of this new band, and it remains unknown whether or not the light absorption corresponding to this band plays an indispensable role in inducing the present photoreactions. The action spectrum would be informative in this connection, but we have not carried out such an experiment.

The intensity of the new band in the **96**–$TiCl_4$ system increased as a function of the time when kept in the dark. Actually, the color of the solution changed from light yellow (immediately after the mixing) to dark yellow, and became dark green after 24 h when kept in the dark. Despite the remarkable color change though, a work-up resulted in the recovery of only the starting ketone. No such color change in the dark was evident in other systems. Even in cases where no coloration was remarkable upon standing in the dark, most of the reactions are accompanied by a color change to some degree during irradiation. Obviously, it seems difficult to characterize the primary light-absorbing species.

The observations described so far provide convincing evidence that both the substrate and the catalyst are involved in the excited species, although a glance at Fig. 1 might lead one to conclude erroneously that the present photoreaction, particularly with Pyrex-filtered light, is induced by the excitation of the catalyst alone.

All these facts favor our previous proposal of a scheme comprising an initial electron transfer, followed by a proton transfer and succeeding cross coupling.[2] All these processes are considered to proceed consecutively within the coordination sphere of metal compounds, thus providing circumstances favorable for the cross coupling. We have no clear-cut interpretation of the different catalytic behavior between titanium(IV) chloride and uranyl chloride. The different mode of coordination could be responsible, but we have no experimental evidence for this argument at the present stage of our investigation.

Addendum. In their synthetic studies of sesquiterpenes, Isoe and his co-workers recently prepared **131** from **130** by means of the titanium(IV) chloride-catalyzed photoreaction, and established the configuration of the introduced hydroxymethyl group in **131** as exclusively *cis* to the methoxycarbonyl group.[56] Although further work should be done for the full interpretation of the stereoselectivity, an explanation of the selectivity can be obtained in terms of our present proposal that the whole reaction proceeds within the coordination sphere of titanium, which, in this case, might coordinate to oxygen atoms of both the ester and carbonyl groups in **130**.



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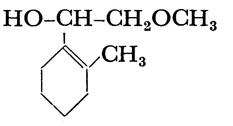

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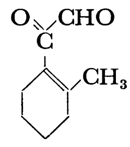

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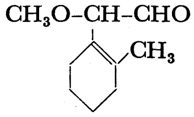

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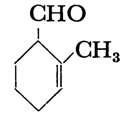

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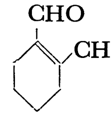

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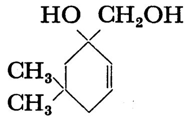

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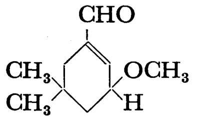

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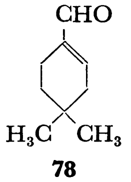

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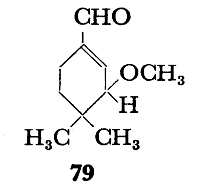

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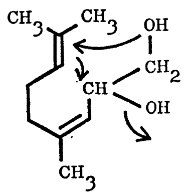

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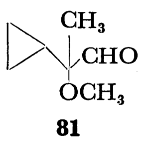

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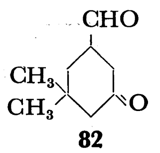

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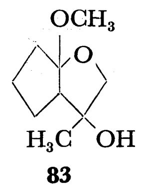

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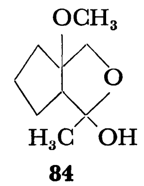

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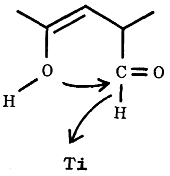

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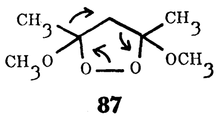

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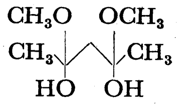

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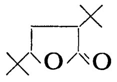

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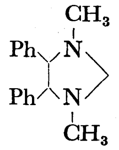

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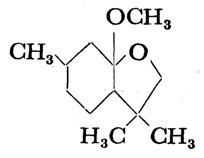

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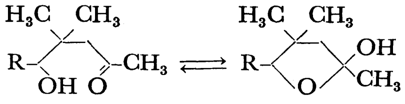
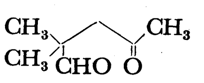
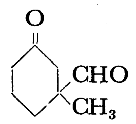


109 **110**



111

a: R=H, b: R=CH$_3$



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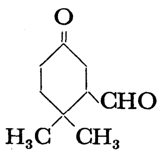

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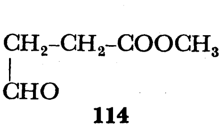
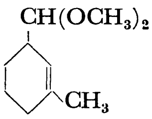


$CH_2\text{-}CH_2\text{-}COOCH_3$ / CHO

114



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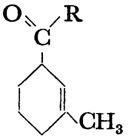

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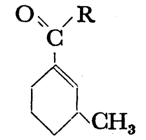

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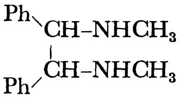
a: R=H d: R=CH$_3$CH$_2$CH$_2$

b: R=CH$_3$ e: R=(CH$_3$)$_2$CH

c: R=CH$_3$CH$_2$



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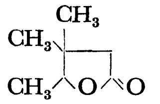

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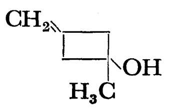

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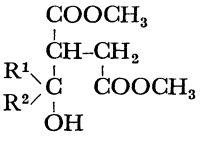

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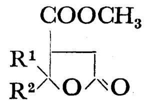

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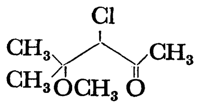

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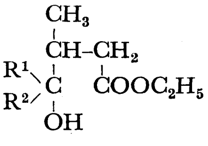
a: R^1=H, R^2=CH$_3$

b: R^1=R^2=CH$_3$



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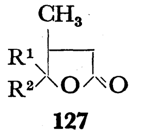

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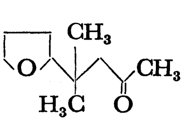

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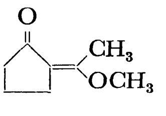

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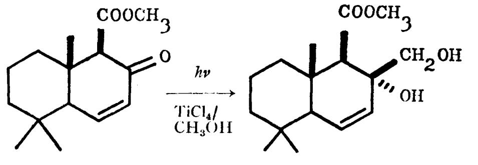

130 **131**

Experimental

General Procedures. The instrumentation was the same as has been described previously.[20] All the irradiations were carried out under the conditions summarized in Table 8, with a high-pressure mercury vapor lamp (Ushio UM 452 (450W)) at the temperature of running water. After the irradiation, the solution was poured into water and shaken with chloroform or dichloromethane. The extract was dried (Na_2SO_4), and the solvent was removed *in vacuo*. The residual substance was treated as indicated in each entry.

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

As for the blank experiments in the presence of hydrochloric acid, a solution in methanol and concd hydrochloric acid (10: 1 by volume) was used.

The yields shown in Tables 1 and 2 were determined on a crude reaction mixture by means of NMR and/or GLC analyses, using appropriate internal references. The isolated yields, when determined, are described in each entry.

Materials. *a) Uranyl Chloride*: Prepared (1) according to the previously reported method[21] or (2) by dissolving thoroughly washed $UO_2(OH)_2$, which had been precipitated from $UO_2(NO_3)_2$ by sodium hydroxide, in hydrochloric acid, evaporating the water, and drying the residue on solid sodium hydroxide under reduced pressure. *b)* **4**: Prepared from cyclopentene and acetyl chloride, using tin(IV) chloride as a condensing reagent, according to the reported procedure[22] with the following modifications. Dichloromethane was used as the solvent at the temperature of Dry Ice, and triethylamine in benzene was used in place of *N,N*-dimethylaniline. Bp 67—69 °C (19 mmHg). *c)* **8**: Prepared from 2-methylcyclohexanone according to the reported procedure,[23] using NBS and pyridine as the brominating and dehydrobrominating reagents respectively. Bp 72—73 °C (22 mmHg). *d)* **10**: Prepared from dimedone (**35**) according to the procedure reported for the preparation of cyclohexenone.[24] Bp 76°C (19 mmHg). *e)* **13**: Ref. 25. Bp 34—38°C (3 mmHg). *f)* **17**: Ref. 26. Bp 44 °C (4 mmHg). *g)* **22**: Commercial sample (*cis* 63% and *trans* 35%). *h)* **29**: Ref. 27. Bp 71—75 °C (20—22 mmHg). *i)* **32**: Ref. 28. Bp 106—110 °C. *j)* **38**: Prepared from 4-(1-cyclopentenyl)morpholine and acetic anhydride according to the procedure reported for the preparation of a six-membered ring homologue.[29] Bp 104—106 °C (12 mmHg). *k)* **44**: Ref. 30. Bp 86 °C (22 mmHg). *l)* **46**: Ref. 31. Bp 85—87 °C (45—50 mmHg). *m)* **48**: Ref. 32. Bp 67 °C (15 mmHg). *n)* **51**: Ref. 33. Bp 97—98 °C (3 mmHg). *o)* **54**: Prepared by stirring an aqueous solution (17.5 ml) of hexanal (5 g) and cyclohexylamine (7.5 g) at room temperature for 2 h. Bp 126—142 °C (30 mmHg). (Lit,[34] bp 115 °C (16 mmHg)). IR, 2960, 2925, 2855, 1665, 1550, 1470, 1450, and 1380 cm^{-1}. NMR, δ 0.6—3.1 (m, 22H) and 7.58 (t, J=8 Hz, 1H). *p)* **57**: Prepared according to the previously reported procedure[35] with the following modifications: methylamine (prepared from 30 g of the hydrochloride) was bubbled into a mixture of acetophenone (10 g) and Molecular Sieve 4A (4 g) in methanol (20 ml) at 60—70 °C. The solution was then decanted from the catalyst and fractionated. *q)* **96**: Ref. 36. Bp 65—66 °C (5 mmHg).

The other materials were commercially available and were subjected to the reaction without further purification.

Run 1. The chromatography of the crude oil on a silica gel column and subsequent purification on a preparative GLC afforded **5**, **6**, and **7** as products, although **6** was not obtained in a highly pure state.

5: MS, *m/e* 125 (M−OMe, base peak), 95, 93, and 67. IR, 3440, 2950, 1370, and 1070 cm^{-1}. NMR, δ 1.30 (s, 3H), 1.6—2.1 (m), 2.1—2.5 (m), 3.10 (s, 3H), 3.28 and 3.52 (ABq, $J=10$ Hz, 2H), and 5.64 (bs, 1H).

6 (in an impure state): IR, no characteristic bands. NMR, δ 0.95 (d, $J=8$ Hz, 3H), 1.5—2.5 (m), 3.21 (s, 3H), 3.24 (s, 3H), 4.10 (d, $J=8$ Hz, 1H), and 5.35 (bs, 1H).

7: (Lit,[37] bp 131—132 °C (140 mmHg)). IR, 2960, 1720, 1360, and 1100 cm^{-1}. NMR, δ 1.4—2.0 (m), 2.15 (s, 3H), 2.83 (bs, 1H), 3.29 (s, 3H), and 3.82 (bs, 1H).

Irradiation in the absence of titanium (IV) chloride afforded a complicated mixture of products irrespective of the presence or absence of hydrochloric acid.

*Oxidation of **5**.* A mixture of CrO_3–pyridine–HCl[38] (0.1 g) and **5** (0.066 g), which had been isolated by preparative TLC (silica gel), in dichloromethane (2 ml) was stirred for 1 h at room temperature. The decanted solution was then passed through a short column of Florisil, and the eluant was evaporated. The crude oil was purified by preparative GLC to give a pure sample of an aldehyde **70**. IR, 2960, 1750, and 1120 cm^{-1}. NMR, δ 1.31 (s, 3H), 1.5—2.5 (m), 3.23 (s, 3H), 5.75 (bs, 1H), and 9.38 (s, 1H).

Run 2. A crude oil (0.37 g) was obtained which was chromatographed on an alumina column to give a fraction (0.22 g) of **9**. MS, *m/e* 170 (M), 140, 139 (base peak), 107, 91, and 79. IR, 3420, 2920, and 1100 cm^{-1}. NMR, δ 1.6—2.3 (m), 1.70 (s, 3H), 3.20 (s, 3H), 3.28 (d of d, $J=11$ and 4 Hz, 1H), 3.49 (d of d, $J=11$ and 8 Hz, 1H), and 4.10 (d of d, $J=8$ and 4 Hz, 1H).

Irradiation in either the presence or absence of hydrochloric acid resulted in the recovery of the starting material.

*Phenylurethane Derivative of **9**.* A mixture of **9** (0.19 g) and phenyl isocyanate (0.13 g) was heated at 60 °C for 5 min. Chromatography on a silica gel column (benzene–chloroform) gave crystals which were subsequently recrystallized from methanol–water. Mp 85 °C. IR, 2920, 1747, 1601, 1520, 1442, and 1205 cm^{-1}. NMR, δ 1.5—2.0 (m), 1.64 (s, 3H), 3.06 (s, 3H), 3.90 (d, $J=8$ Hz, 1H), 3.92 (d, $J=4$ Hz, 1H), and 4.18 (d of d, $J=8$ and 4 Hz, 1H).

Found: C, 70.53; H, 8.00; N, 4.69%. Calcd for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.01; N, 4.84%.

*Treatment of **9** with Hydrochloric Acid.* A mixture of **9** (0.1 g), 3M-hydrochloric acid (15 ml), and ethanol (15 ml) was refluxed for 1.5 h. Subsequent extraction with chloroform gave *o*-ethyltoluene.

*Oxidation of **9**.* The oxidation was carried out in the way described above. A small amount of **73** was obtained, along with the main product **72**. The structure of **72** is not conclusive because the fragmentation pattern of the mass spectrum was not consistent with the structure, although the NMR spectrum was satisfactory. The aldehyde **73** could not be completely freed from **72** by preparative GLC, so the spectrum was obtained by subtracting that of **72** from the spectrum of the mixture.

72: NMR, δ 1.5—1.8 (m, 4H), 2.0—2.3 (bs, 7H), and 9.98 (s, 1H).

73: NMR, δ 1.5—1.8 (m), 1.71 (s, 3H), 1.9—2.3 (m), 3.27 (s, 3H), 4.25 (bs, 1H), and 9.63 (bs, 1H).

Run 3. The oil remaining after the work-up was mainly **11**, accompanied by a small amount of **12**.

11: MS, *m/e* 139 (M−OMe, base peak), 107, 93, 91, 79, and 77. IR, 3400, 2950, and 1100 cm^{-1}. NMR, δ 0.90 (s, 3H), 1.02 (s, 3H), 1.5—1.9 (m, 4H), 3.30 (s, 3H), 3.6—3.9 (b, 1H), 3.90 (bs, 2H), and 5.70 (bs, 1H).

12; IR, 2950, 1708, and 1083 cm^{-1}. NMR, δ 0.88 (s, 3H), 1.10 (s, 3H), 1.15—2.3 (m, 6H), 3.30 (s, 3H), and 3.3—3.7 (m, 1H).

Direct irradiation in methanol resulted in the recovery of the starting material. Irradiation in the presence of hydrochloric acid or a dark reaction in the presence of titanium (IV) chloride gave the methanol adduct **12**.

*Oxidation of **11**.* An oxidation and work-up in the way described above afforded an aldehyde **77**. MS, *m/e* 168 (M), 139 (base peak), 107, 91, and 79. IR, 2950, 2820, 2700, 1688, 1210, and 1102 cm^{-1}. NMR, δ 0.87 (s, 3H), 1.02 (s, 3H), 1.2—2.3 (m), 3.37 (s, 3H), 3.8—4.1 (b, 1H), and 9.48 (s, 1H).

Run 4. A crude oil was distilled at 4 mmHg into four fractions. Each fraction was found by GLC analyses to contain one or two of the products **14**—**16**. The isolated yields of the products were 12% for **14**, 3% for **15**, and 2% for **16**.

14: MS, *m/e* 170 (M), 139, and 114 (base peak). IR, 3420, 2920, 1209, and 1090 cm^{-1}. NMR, δ 0.85 (s, 3H), 0.95 (s, 3H), 1.0—2.0 (m), 3.22 (bs, 1H), 3.37 (s, 3H), 3.96 (bs, 2H), and 5.67 (bs, 1H).

15: MS, *m/e* 153 (M−OMe), 137, 121, 105, 93, 91, and 75 (base peak). IR, 2950, 1120, and 1055 cm^{-1}. NMR, δ 1.02 (s, 6H), 1.1—2.5 (m), 3.30 (s, 3H), 3.33 (s, 3H), 3.99 (d, $J=9$ Hz, 1H), and 5.47 (s, 2H).

Found: C, 71.46; H, 10.71%. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94%.

16: MS, *m/e* 156 (M), 141, 125, 100, 87, 75, and 70 (base peak). IR, 2920, 1720, and 1100 cm^{-1}. NMR, δ 1.02 (s, 3H), 1.10 (s, 3H), 1.2—1.6 (m, 1H), 1.6—1.9 (m, 1H), 2.1—2.6 (m, 4H), 3.03 (d of d, $J=8$ and 5 Hz, 1H), and 3.28 (s, 3H).

A dark reaction in the presence of titanium(IV) chloride gave **16** in 63% yield. Irradiation in either the presence or absence of hydrochloric acid gave a complicated mixture of products.

*Oxidation of **14**.* The oxidation of **14** in the way described above afforded an aldehyde **79**. MS, *m/e* 168 (M), 112, and 83. IR, 2940, 2820, 2720, 1680, 1640, 1190, and 1095 cm^{-1}. NMR, δ 0.82 (s, 3H), 1.02 (s, 3H), 1.4—1.7 (m, 2H), 2.1—2.3 (m, 2H), 3.50 (s, 4H), 6.67 (bs, 1H), and 9.56 (s, 1H). The signal at δ 3.50 split into a three-proton singlet and a one-proton signal upon the addition of $Eu(FOD)_3$.

*Hydrolysis of **15**.* The acetal **15** was treated with 3M-hydrochloric acid in methanol in the way described above to give an aldehyde **78**. MS, *m/e* 138 (M), 123, 109, and 95 (base peak). IR, 2960, 1680, and 1640 cm^{-1}. NMR, δ 1.00 (s, 6H), 1.4—1.6 (m, 2H), 2.0—2.5 (m, 4H), 6.73 (bs, 1H), and 9.57 (s, 1H).

Run 5. The work-up and preparative GLC afforded a pure sample of **18**. MS,[39] *m/e* 134 (M), 133 (base peak), 105, 91, 79, and 77. IR, 2930, 2840, 2720, 1690, 1610, and 1110 cm^{-1}. NMR, δ 2.36 (s, 6H), 7.21 and 7.53 (ABq, $J=9$ Hz, 2H), 7.57 (s, 1H), and 9.85 (s, 1H). These NMR data are not consistent with those of 2,4-[40] or 2,5-[41] dimethylbenzaldehyde.

No reaction occurred in the dark in the presence of titanium(IV) chloride. Irradiation in methanol in either the presence or absence of hydrochloric acid gave a complicated mixture of products.

Run 6. The work-up afforded an oil which was an almost pure sample of **20**, accompanied by a small amount of **21**, as revealed by GLC and NMR analyses. The same products were obtained when titanium(IV) chloride was used as the catalyst, but, in this case, the amount of the by-product **21** was much greater.

20: MS, *m/e* 85 (M−OMe, base peak), 71, 56, and 41. IR, 3060, 1450, 1370, 1100, and 1030 cm^{-1}. NMR, [δ 0.98 (d,

J=8 Hz, for *trans*) and 1.02 (d, J=8 Hz, for *cis*)] 3H, 1.3—1.5 (m, 1H), 1.7—2.5 (m, 2H), [3.03 (s, for *trans*) and 3.06 (s, for *cis*)] 3H, 3.15 (t, J=8 Hz, 1H), [3.65 (t, J=8 Hz, for *cis*) and 3.75 (t, J=8 Hz, for *trans*)] 1H, and 4.60 (d, J=5 Hz, 1H). The signal assignments for the *cis*-and *trans*-isomers were performed by adding Eu(DPM)$_3$. From the intensities of the methyl signals, the ratio of the *cis*- to the *trans*-isomer was determined to be 42: 58.

Found: C, 61.59; H, 10.16%. Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.41%.

21: NMR, δ 1.05 (d, J=6 Hz, 3H), 1.45—1.55 (m, 2H), 3.10 (s, 9H), 3.1—3.2 (m), and 4.26 (d of d, J=4 and 3 Hz, 1H).

The irradiation of **19** in the presence of hydrochloric acid gave **21** as the exclusive product. The direct irradiation gave an oil which is considered from its NMR spectrum to be a mixture of *cis*- and *trans*-**19**, as well as their dimethyl acetals.

Run 7. The oil remaining after the work-up was distilled under reduced pressure to give a mixture of **23**—**25**. Each component was separated by preparative GLC.

23: MS, *m/e* 166 (M), 151, 136, 121, 108, and 93 (base peak). IR, 2950, 1460, 1380, 1170, and 1050 cm^{-1}. NMR, δ 1.0—2.0 (m), 1.14 (s, 6H), 1.68 (s, 3H), 3.33 (d of d, J=9 and 8 Hz, 1H), 3.90 (t, J=8 Hz, 1H), and 5.37 (bs, 1H).

24: The NMR data coincided with the reported data.[42]

25:[43] IR, 2960, 1620, 1360, 1250, 1160, and 1060 cm^{-1}. NMR, δ 1.49 (s, 6H), 2.40 (s, 3H), 3.07 (s, 3H), 7.04 and 7.18 (ABq, J=9 Hz, 4H).

The dark reaction in the presence of titanium(IV) chloride gave **24** and **25** in 31% and 10% yields respectively. Irradiation in either the presence or absence of hydrochloric acid gave a complicated mixture of products.

Run 8. The work-up afforded an oil which was identified by NMR analysis as a mixture of **27** and **28** (66: 34). Details concering the data will be described in Run 29. A dark reaction in the presence of titanium(IV) chloride resulted in the recovery of the starting material.

Run 9. The oil remaining after the work-up was an almost pure sample of **30**, accompanied by a small amount of **31**, as revealed by GLC analysis.

30: IR, 3080, 3000, 2920, 2840, 1470, 1360, and 1080 cm^{-1}. NMR, δ 0.0—0.9 (m, 11H), 3.35 (s, 6H), and 4.15 (d, J=5 Hz, 1H).

Found: C, 69.97; H, 10.32%. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66%.

The aldehyde **31** was identical with an authentic sample prepared according to the reported method.[44]

Irradiation in either the presence or absence of hydrochloric acid gave a complicated mixture of products.

*Preparation of **30**.* A mixture of **31** (0.27 g), methyl orthoformate (0.5 g), and ammonium nitrate (0.025 g) in methanol (0.5 ml) was kept at room temperature for 8 h. A saturated solution of sodium carbonate was then added, and the solution was shaken with dichloromethane. The subsequent evaporation of the solvent from the extract left an oil which was identical with **30**.

Run 10. The oil remaining after the work-up was almost pure **33**, accompanied by a small amount of **34**, as revealed by NMR and GLC analyses.

33: MS, *m/e* 99 (M−OMe, base peak), 69, 67, and 41. IR, 3670, 3590, 3070, 1480, 1400, 1080, and 1050 cm^{-1}. NMR, δ 0.0—1.0 (m, 5H), 0.85 (s, 3H), 2.45 (bs, 1H, disappears by D_2O), 3.15 (s, 3H), and 3.20 and 3.30 (ABq, J=11 Hz, 2H).

Found: C, 64.23: H, 11.33%. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84%.

34: MS, *m/e* 113 (M−OMe), 81, 75 (base peak), and 47 IR, 2960, 2920, 2820, 1450, 1380, and 1070 cm^{-1}. NMR, δ 0.0—0.7 (m, 5H), 0.7—1.1 (m, 4H), 3.12 (s, 6H), and 3.85 (d, J=7 Hz, 1H). The multiplet at δ 0.7—1.1 split into a three-proton doublet (J=8 Hz) and a one-proton distorted sextet (J=7—8 Hz) upon the addition of Eu(DPM)$_3$.

Found: C, 65.75; H, 11.30%. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18%.

When the photolysate was refluxed for 30 min and then worked-up in the same way as above, **34** was obtained as the sole product. The irradiation of **32** in methanol in either presence or absence of hydrochloric acid gave a complicated mixture of products.

*Oxidation of **33**.* The oxidation of **33** in the way described above gave an aldehyde **81**. IR, 3030, 2970, 2830, 1740, and 1090 cm^{-1}. NMR, δ 0.2—1.0 (m, 5H), 1.10 (s, 3H), 3.23 (s, 3H), and 9.45 (s, 1H).

*Phenylurethane Derivative of **33**.* The phenylurethane derivative of **33** was prepared in the way described in Run 2. Although the product seems to be pure, judging from its NMR spectrum, we could not effect the crystallization. NMR (in an impure state), δ 0.05—0.6 (m, 4H), 0.7—1.0 (m, 1H), 0.86 (s, 3H), 3.00 (s, 3H), 3.85 (s, 2H), 6.5—7.1 (m, 5H), and 7.18 (bs, 1H).

Run 11. The oil remaining after the work-up was a mixture of **36** and **37**, judging from the GLC and NMR analyses.

36: MS, *m/e* 169 (M−OMe), 153, 125, 97, and 74 (base peak). IR, 2950, 1700, 1120, and 1050 cm^{-1}. NMR, δ 0.95 (s, 3H), 1.15 (s, 3H), 1.3—2.5 (m, 7H), 3.35 (s, 6H), and 4.10 (d, J=6 Hz, 1H).

The enol ether **37** was identical with a sample prepared according to the reported method.[45]

When **36** was treated with 2,4-dinitrophenylhydrazine, the bis(2,4-dinitrophenylhydrazone) of the keto aldehyde **82** was obtained; it was subsequently recrystallized from dioxane-methanol. Mp 210—212 °C.

Found: C, 48.64; H, 4.13; N, 21.35%. Calcd for $C_{21}H_{22}N_8O_8$: C, 49.03; H, 4.31; N, 21.78%.

*Hydrolysis of **36**.* A crude sample of **36** was refluxed in a mixture of methanol (10 ml) and conc. hydrochloric acid (4 ml) for 4 h. The solution was then diluted with water and extracted with chloroform. The subsequent evaporation of the solvent from the extract left an oil which was purified by preparative GLC to give **82**. MS, *m/e* 139 (M−Me), 126, 83, 69, 57, 55 (base peak), and 41. IR, 2930, 1710, and 1250 cm^{-1}. NMR, δ 0.92 (s, 3H), 1.12 (s, 3H), 1.3—2.8 (m, 7H), and 9.50 (d, J=0.5 Hz, 1H).

*Irradiation of **37** in the Presence of Titanium(IV) Chloride.* Irradiation was carried out under the same conditions as those used with **35**. An acetal **36** was obtained as the sole product.

Run 12. The oil remaining after the work-up was distilled under reduced pressure to give a pure sample of **39**. Bp 58—62 °C (15 mmHg), 0.1 g. MS, *m/e* 172 (M), 157, 155, 143, and 141 (base peak). IR, 3510, 2930, 1770 (weak), 1450, 1400, 1370, 1320, 1200, and 1020 cm^{-1}. NMR, δ 1.15 (s, 3H), 1.1—2.2 (m, 7H), 3.30 (s, 3H), and 3.73 and 3.82 (ABq, J=7 Hz, 2H).

Found: C, 62.67; H, 9.09%. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36%.

When **38** was irradiated in methanol without any additives, or when it was kept in methanol-hydrochloric acid in the dark, it gave an enol ether **129**. IR, 2950, 1740, 1720, 1435, 1360, and 1165 cm^{-1}. NMR, δ 1.45—1.65 (m), 2.05 (s, 3H), 2.1—2.5 (m), and 3.56 (s, 3H).

Run 13. The oil remaining after the work-up was distilled under reduced pressure. An oil, bp 39—45 °C (15 mmHg), was thus obtained which was found by GLC analysis to be a mixture of several compounds; three major fractions (**41**—**43**) were collected in pure states by preparative GLC (temperature, 70 °C).

41: MS, *m/e* 112 (M), 111, 97, and 69 (base peak). The IR and NMR spectra were identical with those previously reported.[4)]

42: Identical with the authentic sample prepared according to the reported method.[5)]

43: IR, 2940, 1450, 1370, 1320, 1180, and 1050 cm^{-1}. NMR, δ 1.45 (s, 6H), 2.60 (s, 2H), and 3.35 (s, 6H).

Found: C, 52.26; H, 9.00%. Calcd for $C_7H_{14}O_4$: C, 51.84; H, 8.70%.

Irradiation of **40** *in the Presence of Hydrochloric Acid.* A solution of **40** (0.1 g) and concd hydrochloric acid (0.4 ml) in methanol (10 ml) was irradiated in a Pyrex tube for 24 h. The subsequent evaporation of the extract left **43** in an almost pure state (GLC and NMR analyses). The temperature of the GLC should not exceed 70 °C.

Thermolysis of **43**. When a neat sample of **43** was kept at 150 °C for 2 h, an equimolar mixture of methyl acetate and methyl propionate was obtained, as established by GLC and NMR techniques.

Run 14. The crystals obtained after the work-up (0.26 g) were almost pure **45**. Recrystallization from carbon tetrachloride gave white needles; mp 91—92 °C (lit,[4)] mp 92—94 °C). The IR and NMR data coincided with the reported values.[4)] Hydrogenation over Pd/C gave **89**, which also indicated IR and NMR spectra identical with those previously reported.[4)] Mp 73—75 °C (lit, mp 86—88 °C,[4)] or 82—83 °C.[46)])

Run 15. The oil remaining after the work-up was a mixture of **47** and one more product of an unknown structure. **47**: IR, 2980, 2925, 1760, 1440, 1090, and 1000 cm^{-1}. NMR, δ 1.36 (d, J=7 Hz, 3H), 1.75 (s, 3H), 1.95 (s, 3H), and 4.68 (q, J=7 Hz, 1H).

Run 16. The photolysate was diluted with water and made alkaline with a sodium hydroxide solution. The precipitates of titanium hydroxide were filtered off with the aid of Hyflo Super Cel, and the filtrate was shaken with dichloromethane. The subsequent evaporation of the solvent from the extract left an oil which was found by NMR analysis to be a mixture of **49** and **50** (4: 1). Distillation under reduced pressure gave **49** in an almost pure state. Bp 125—133 °C (6 mmHg), 0.75 g, 59%. (Lit,[47)] bp 115—120 °C (4 mmHg)). NMR, δ 2.25 (s, 3H), 3.72 (bs, 2H), 4.72 (bs, 2H), and 7.2—7.7 (m, 5H).

When the crude material of **49** was treated with *p*-nitrobenzoyl chloride in benzene, crystals of bis (*p*-nitrobenzoyl) derivative were obtained. Recrystallization from chloroform-ethanol afforded a pure sample. Mp 167—168 °C.

Found: C, 60.94; H, 4.19; N, 8.99%. Calcd for $C_{23}H_{19}N_3O_7$: C, 61.47; H, 4.26; N, 9.35%.

The picrate of **49** was also obtained. Recrystallization from ethanol afforded a pure sample. Mp 188—191 °C.

Found: C, 46.74; H, 4.04; N, 14.46%. Calcd for $C_{15}H_{16}N_4O_8$: C, 47.37; H, 4.24; N, 14.73%.

Preparation of **50**. An appropriate amount of 37% formalin was added to the photolysate of **48**, and the solution was kept at room temperature for 7 days. The work-up described above afforded an oil which was almost pure **50**. IR, 2880, 2800, 1495, 1455, and 1070 cm^{-1}. NMR, δ 2.30 (s, 3H), 3.53 and 3.67 (d (J=8 Hz) of ABq, J=8 Hz, 2H), 4.08 (d, J=2 Hz, 1H), 4.25 (t, J=8 Hz, 1H), 4.78 (d, J=2 Hz, 1H), and 7.2—7.7 (m, 5H). The signals at δ 3.53 and 3.67 separated into two one-proton triplets (J=8 Hz) upon the addition of $Eu(DPM)_3$.

Run 17. The work-up described in Run 16 afforded crystals of **52**; 0.52 g, mp 87—95 °C. Recrystallization from carbon tetrachloride–hexane afforded a pure sample. Mp 107—109 °C. IR, 3400, 3120, 1445, 1055, and 1030 cm^{-1}. NMR, δ 0.9—1.4 (m, 5H), 1.4—1.8 (m, 4H), 1.8—2.1 (b, 1H), 2.2—2.5 (b, 1H), 2.40 (bs, 2H, disappears by D_2O), 3.48 [d (J=11 Hz) of AB (J=10 Hz), 1H], 3.70 [d (J=4 Hz) of AB (J=10 Hz), 1H], 3.96 (d of d, J=11 and 4 Hz, 1H), and 7.2—7.6 (m, 5H).

Found: C, 75.97; H, 9.57; N, 6.18%. Calcd for $C_{14}H_{21}NO$: C, 76.66; H, 9.65; N, 6.39%.

Preparation of **53**. A mixture of **52** (0.031 g) and 37% formalin (0.018 g) in methanol (0.5 ml) was stirred at 70 °C for 6 h. The work-up afforded a crude sample of **53**. NMR, δ 1.0—2.0 (m, 10H), 2.1—2.7 (bs, 1H), 3.5—3.7 (m, 1H), 4.0—4.3 (m, 2H), 4.5—4.75 (m, 2H), and 7.2—7.6 (m, 5H).

Run 18. The work-up described in Run 16 afforded a crude oil (0.34 g), which partly crystallized upon standing. The crystals were collected and recrystallized from carbon tetrachloride to give white needles of **55**. Mp 71—73 °C. IR (KBr), 3420, 3260, 2960, 2925, 2850, 1450, 1360, 1140, and 1120 cm^{-1}. NMR ($CDCl_3$), δ 0.77—2.1 (m, 2H), 2.07 (bs, 2H, disappears by D_2O), 2.35—2.88 (m, 2H), 3.20 [d (J=7 Hz) of AB (J=11 Hz), 1H], and 3.58 [d (J=4 Hz) of AB (J=11 Hz), 1H].

From the mother liquor separated from the crystals of **55**, a pure sample of **56** was obtained by preparative GLC. MS, *m/e* 225 (M), 194, 182, 154 (base peak), 72, and 55. IR, 2960, 2925, 2855, 1470, 1450, 1375, 1170, and 1028 cm^{-1}. NMR, δ 0.76—2.11 (m, 21H), 2.17—2.57 (m, 1H), 2.89—3.28 (m, 2H), 3.78 (t, J=7 Hz, 1H), and 4.15 and 4.42 (ABq, J=6 Hz, 2H).

Irradiation without any additive or a dark reaction in the presence of titanium(IV) chloride resulted in the recovery of the starting material. Irradiation in the presence of hydrochloric acid afforded a complicated mixture of products.

Run 19. The work-up described in Run 16 afforded a mixture of **58** and **59** (3: 2), as revealed by the NMR spectrum. When the mixture and 37% formalin (0.19 g) in methanol (0.5 ml) were kept at 70 °C for 2 h, and then at room temperature overnight, **59** was obtained; it was identical with the sample obtained in Run 21. The NMR spectrum of **58** was obtained by subtracting that of **59** from the mixture spectrum. δ 1.43 (s, 3H), 2.14 (s, 3H), 3.0—3.6 (b), 3.39 (s), and 7.2—7.6 (m).

Run 20. The work-up afforded white crystals (0.2 g). Recrystallization from methanol afforded white needles of **61**. Mp 122—127 °C. (Lit,[48)] mp 125 °C). MS, *m/e* 144 (M—MeOH, base peak), 113, and 73. IR (KBr), 1370, 1285, 1196, 1175, 1065, and 1035 cm^{-1}. NMR, δ 1.15 (s, 6H), 3.20 (s, 6H), and 3.27 and 3.50 (ABq, J=11 Hz, 4H).

Found: C, 55.18; H, 9.59%. Calcd for $C_8H_{16}O_4$: C, 54.53; H, 9.15%.

It was speculated that the crude crystals contain a stereoisomer of **61** (one-third of **61**), since these crystals indicated NMR signals at δ 1.30 (s, 6H), 3.22 (s, 6H), and 3.27 and 3.50 (ABq, J=11 Hz, 4H, overlap with those of **61**), as well as those of **61**.

Compound **61** was identical with the crystals separated out from a 50% methanol solution of hydroxyacetone.

Run 21. The photolysate was made alkaline with a sodium hydroxide solution, and the solid was filtered off (Hyflo Super Cel). The filtrate was made acidic with hydrochloric acid and shaken with chloroform (Extract A). The aqueous solution was made alkaline with sodium hydroxide solution again, and shaken with chloroform (Extract B). Extract A, upon the evaporation of the solvent, gave a trace amount of an oil from which two products, **63** and **64**, were obtained in pure states by preparative GLC. Compound **63** was identical with the authentic sample. **64**: IR (neat), 3450, 1610, 1505, 1455, 1030, 760, and 695 cm^{-1}. NMR, δ 1.35 (s, 3H), 2.4—2.9 (b, 2H), 3.26 and 3.45 (ABq, J= 11 Hz, 2H), and 6.8—7.1 (m, 5H).

Compound **64** was identical with the sample obtained in a small amount by the irradiation of acetophenone (0.12 ml) in methanol (12 ml) in the presence of titanium(IV) chloride (0.12 ml).

Extract B, upon the evaporation of the solvent, gave an oil which was subsequently distilled under reduced pressure to give 0.13 g of **59**. MS, *m/e* 177 (M), 162 (base peak), 146, 132, and 91. IR (neat), 2980, 2850, 2780, 1440, 1050, 758, and 690 cm^{-1}. NMR δ 1.35 (s, 3H), 2.05 (s, 3H), 3.52 and 3.65 (ABq, J=8 Hz, 2H), 4.07 and 4.27 (dist. ABq, J=2 Hz, 2H), and 6.7—7.2 (m, 5H).

Found: C, 73.82; H, 8.30; N, 7.75%. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90%.

Run 22. The photolysate was worked-up in the way described in Run 21. A trace amount of **67** was obtained from the extract from the acidic solution. The amount of the product corresponding to **64** was negligible. **67**: IR (neat), 3320, 2960, 1510, 1440, 1360, 1065, 1005, 890, and 810 cm^{-1}. NMR, δ 1.39 (d, J=7 Hz, 3H), 2.25 (s, 3H), 4.55 (q, J=7 Hz, 1H), and 6.78 and 6.90 (ABq, J=8 Hz, 4H).

The extract from the alkaline solution gave an oil which was subsequently distilled under reduced pressure to give 0.062 g of **66**. IR (neat), 3380, 2950, 2880, 1520, 1460, 1380, 1083, 1018, and 812 cm^{-1}. NMR, δ 1.35 (s, 3H), 2.21 (s, 3H), 3.43 and 3.52 (ABq, J=7 Hz, 2H), 4.03 and 4.23 (ABq, J=6 Hz, 2H), and 6.70 and 6.88 (ABq, J=8 Hz, 4H).

Found: C, 74.54; H, 8.82; N, 7.85%. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90%.

Run 23. The work-up was the same as that described in Run 21. The amounts of products corresponding to **63** and **64** were negligible. The extract from the alkaline solution gave an oil which was subsequently distilled under reduced pressure to give 0.088 g of **69**. MS, *m/e* 176 (M−1), 162, 147, 146 (base peak), 133, 132, 105, and 91. IR (neat), 2980, 2890, 1450, 1080, 1015, 900, and 758 cm^{-1}. NMR, δ 1.40 (s, 3H), 2.27 (s, 3H), 3.44 and 3.74 (ABq, J=7 Hz, 2H), 4.06 and 4.30 (ABq, J=6 Hz, 2H), 6.65—6.85 (m, 3H), and 7.17—7.35 (m, 1H).

Found: C, 74.62; H, 8.76; N, 7.71%. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90%.

Run 24. The oil remaining after the work-up indicated a complicated NMR spectrum suggestive of the structure **108** of a stereoisomeric mixture. Distillation induced the elimination of methanol from these isomers and gave **92** in an almost pure state; bp 72—78 °C (23 mmHg). IR, 2930, 1710 (weak), 1463, 1172, 1120, and 980 cm^{-1}. NMR, δ 0.97 (d, J=8 Hz, 3H), 1.00 (s, 6H), 1.5—2.1 (m, 7H), and 3.64 (s, 2H).

Found: C, 78.67; H, 11.23%. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

Run 25. The oil remaining after the work-up was distilled to give **20** (bp 56—65 °C (25 mmHg)), which contained a small amount of chloroform. The IR and NMR spectra were identical with those obtained in Run 6.

Run 26. The oil remaining after the work-up was distilled to give **94** (bp 35—56 °C (3 mmHg)), which contained a small amount of chloroform. MS, *m/e* 113 (M−OMe, base peak), 112, and 97. IR, 2965, 2885, 1470, 1378, 1190, 1050, and 1028 cm^{-1}. NMR, δ 1.00 (s, 3H), 1.05 (s, 3H), 1.25 (s, 3H), 1.50 and 1.70 (ABq, J=13 Hz, 2H), 2.96 (s, 3H), and 3.23 and 3.30 (ABq, J=8 Hz, 2H).

From the crude oil prior to the distillation, a small amount of **95**[10] was isolated by preparative GLC. MS, *m/e* 142 (M), 100, 99, 85 (base peak), 82, and 43. IR, 2960, 1715, 1700, 1360, 1170, and 1130 cm^{-1}. NMR, δ 1.15 (s, 6H), 2.00 (s, 3H), 2.10 (s, 3H), and 2.60 (s, 2H).

When **94** was kept in a mixture of tetrahydrofuran–3M-hydrochloric acid (2: 1) at room temperature for 10 min, an oil was obtained which was identified from its NMR spectrum as a mixture of **109a** and **110a**. The oxidation of the oil with CrO_3–pyridine–HCl in the way described above afforded keto aldehyde **111**. MS, *m/e* 100 (M−CO), 85, and 43 (base peak). IR, 2960, 2800, 2650, 1725, and 1370 cm^{-1}. NMR, δ 1.10 (s, 6H), 2.10 (s, 3H), 2.65 (s, 2H), and 9.60 (s, 1H).

Run 27. The oil remaining after the work-up was a mixture of **97** and **99**, as revealed by NMR analysis. Distillation under reduced pressure induced the elimination of methanol from **99** and gave a mixture of the starting material and **97** (bp 68—94 °C (18 mmHg), 0.66 g). On some occasions, the product contained **98** (0—10% of **97**).

97: MS, *m/e* 156 (M), 141, 125, 113 (base peak), and 111. IR, 2990, 2900, 1457, 1195, 1105, 1030, and 1012 cm^{-1}. NMR δ 0.98 (s, 3H), 1.05—2.25 (m, 8H), 3.05 (s, 3H), and 3.30 and 3.40 (ABq, J=6 Hz, 2H).

98: MS, *m/e* 142 (M), 125, 112, 111 (base peak), and 99. IR, 3400, 1710, 1230, and 1050 cm^{-1}. NMR, δ 0.90 (s, 3H), 1.7—2.4 (m, 8H), and 3.25 (s, 2H).

99: IR, 2960, 2870, 1715, 1213, 1112, and 1065 cm^{-1}. NMR, δ 1.15 (s, 3H), 1.5—2.5 (m, 8H), and 3.00 (s, 3H).

Found: C, 66.79; H, 9.95%. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93%.

No reaction occurred in the dark in the presence of uranyl chloride. Irradiation in methanol in the presence of an ordinary amount of hydrochloric acid resulted in the recovery of the starting ketone, while in the presence of a small amount of hydrochloric acid (pH 2—3), a methanol adduct **99** was obtained exclusively.

*Oxidation of **98**.* The oxidation of **98** in the way described above afforded an aldehyde **112**. MS, *m/e* 112 (M−CO), 111, 97, 83, 69, and 55 (base peak). IR, 2960, 2800, 2650, 1720, and 1220 cm^{-1}. NMR, δ 1.11 (s, 3H), 1.2—2.6 (m), and 9.34 (s, 1H).

Run 28. The work-up left an oil which was distilled under reduced pressure to give two fractions: Fraction 1 (bp 36—41 °C (1 mmHg), 0.17 g) contained 32% of **100**, while Fraction 2 (bp 62—68 °C (1 mmHg), 0.22 g) contained 51% of **101**, as revealed by GLC analyses.

100: MS, *m/e* 170 (M), 139, 125, 110, 100, and 99 (base peak). IR, 2960, 1310, 1190, and 1120 cm^{-1}. NMR, δ 0.97 (s, 3H), 1.02 (s, 3H), 1.1—2.0 (m), 3.24 (s, 3H), and 3.89 (m, 2H). The multiplet at δ 3.89 was transformed into a typical ABX type upon the addition of Eu(DPM)$_3$.

Found: C, 70.03; H, 10.50%. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66%.

101: MS, *m/e* 156 (M), 126, 125, 85, 83, 69, and 55 (base peak). IR, 3440, 2940, and 1710 cm^{-1}. NMR, δ 1.08 (s, 3H), 1.16 (s, 3H), 0.9—2.6 (m), and 3.3—3.9 (m, 2H).

*Oxidation of **101**.* The oxidation of **101** in the way described above afforded an aldehyde **113**. MS, *m/e* 154 (M), 126, 111, 97, 83, 69, and 55 (base peak). IR, 2960 and 1730 cm^{-1}. NMR, δ 1.14 (s, 3H), 1.31 (s, 3H), 1.6—1.9 (m, 2H), 2.1—2.7 (m, 5H), and 9.98 (s, 1H).

Run 29. An oil (bp 108—110 °C (3.5 mmHg), 0.84 g) was obtained which was found by NMR analysis to be a mixture of **27** and **28** (93: 7). Further purification was not achieved, so the spectroscopic data of **27** were obtained by subtracting those of **28** from the spectra of the mixture. **27**: IR: 3440, 2920, 1740, and 1450 cm^{-1}. NMR, δ 2.57 and

2.64 (d of d, J=7 and 5 Hz, 2H), 2.8—3.0 (m, 1H), 3.30 (bs, 1H), 3.67 (bs, 3H+2H), and 3.70 (s, 3H).

When the mixture was kept at 200 °C for 1 h, **28**[49] was obtained in a 60% yield. Bp 96—97 °C (1.5 mmHg). IR, 1795, 1745, 1450, 1165, and 1015 cm^{-1}. NMR, δ 2.70 (d, J=10 Hz, 1H), 2.71 (d, J=7.5 Hz, 1H), 3.45 (dist. quintet, J=8 Hz, 1H), 3.78 (s, 3H), 4.40[d (J=7 Hz) of AB (J=10 Hz), 1H], and 4.51[d (J=9 Hz) of AB (J=10 Hz), 1H].

Found: C, 49.24; H, 5.63%. Calcd for $C_6H_8O_4$: C, 50.00; H, 5.60%.

Run 30. An oil (bp 63—67 °C (3 mmHg), 1.04 g) was obtained which was found by NMR analysis to be a mixture of **103** and **104** (84: 16). Further purification was not achieved, and so the spectroscopic data of **103** were obtained by subtracting those of **104** from the spectra of the mixture. **103**: IR, 3490 and 1740 cm^{-1}. NMR, δ 0.90 (d, J=7 Hz, 3H), 1.85—2.56 (m), 3.35 (bs, 1H, disappears by D_2O), 3.36 (dist. quintet, J=6 Hz, 2H), and 3.57 (s, 3H).

When **103** was kept at 200 °C for 3 h, **104** was obtained. Bp 56—57 °C (3 mmHg) (lit,[50] bp 80—81 °C (10 mmHg)). IR, 2990, 1790, 1165, and 1025 cm^{-1}. NMR, δ 1.11 (d, J=7 Hz, 3H), 1.8—2.2 (m, 1H), 2.4—2.8 (m, 2H), 3.74 (d of d, J=9 and 7 Hz, 1H), and 4.29 (d of d, J=10.5 and 9 Hz, 1H).

Run 31. The oil remaining after the work-up was distilled under reduced pressure. Much of a colorless, viscous material remained undistilled. The distillate (bp 62—65 °C (2 mmHg), 0.28 g) was found by NMR analysis to be a mixture of **106** ans **107** (94: 6). Further purification was not achieved, and so the spectroscopic data of **106** were obtained by subtracting those of **107** from the spectra of the mixture. **106** (lit,[51] bp 45—46 °C (0.2 mmHg)): IR, 3420 and 1745 cm^{-1}. NMR, δ 1.80 (quintet, J=7 Hz, 2H), 2.38 (t, J=7 Hz, 2H), 3.23 (bs, 1H), 3.58 (t, J=7 Hz, 2H), and 3.63 (s, 3H).

Found (with a sample of 94% purity): C, 50.69; H, 8.72%. Calcd for $C_5H_{10}O_3$: C, 50.83; H, 8.53%.

When **106** was kept at 200 °C for 3 h, **107** was obtained in a pure state; it was identical with γ-butyrolactone.

*Oxidation of **106**.* The oxidation of **106** in the way described above afforded an aldehydic ester **114**. (Lit,[52] bp 79—80 °C (12 mmHg)). MS, *m/e* 88 (M—CO), 85, 59, and 57. IR, 2960, 2820, 2710, 1740, 1440, and 1175 cm^{-1}. NMR, δ 2.5—2.9 (A_2B_2m, 4H), 3.70 (s, 3H), and 9.95 (s, 1H).

*Irradiation of 3-Methyl-2-cyclohexenone (**96**) in Alcohols in the Presence of Titanium(IV) Chloride.* Solutions of **96** (0.1 g) and titanium(IV) chloride (0.17 g) in the following alcohols (10 ml) were irradiated in Pyrex tubes for 6 h. Subsequent work-ups afforded oils which were analyzed by GLC and NMR to determine the yields.

In 1-Propanol: The product was **116c**. MS, *m/e* 152 (M), 95 (base peak), 79, 77, and 67. IR, 2900, 1710, 1440, and 1110 cm^{-1}. NMR, δ 1.03 (t, J=8 Hz, 3H), 1.3—2.0 (b, 6H), 1.70 (bs, 3H), 2.41 (q, J=8 Hz, 2H), 2.94 (b, 1H), and 5.47 (bs, 1H).

In 1-Butanol: The products were **116d** and **117d**.

116d: MS, *m/e* 166 (M), 95 (base peak), 79, 77, 71, and 67. IR, 2920, 1710, and 1130 cm^{-1}. NMR, δ 0.91 (t, J=8 Hz, 3H), 1.0—2.2 (m), 1.68 (bs, 3H), 2.34 (t, J=8 Hz, 2H), 2.92 (b, 1H), and 5.48 (bs, 1H).

117d: IR, 2950, 2930, 1670, and 1200 cm^{-1}. NMR, δ 0.92 (t, J=8 Hz, 3H), 1.13 (d, J=8 Hz, 3H), 1.2—2.0 (m), 2.52 (t, J=8 Hz, 2H), and 6.51 (bs, 1H).

In 2-Methyl-1-propanol: The product was **116e**. MS, *m/e* 166 (M), 95 (base peak), 79, 77, 71, and 67. IR, 2960, 2930, and 1710 cm^{-1}. NMR, δ 1.06 (d, J=8 Hz, 6H), 1.5—2.0 (m), 1.70 (bs, 3H), 2.72 (heptet, J=8 Hz, 1H), 3.10 (b, 1H), and 5.45 (bs, 1H).

In 2-Propanol: The product was *m*-cymene. IR,[53] 2950, 2910, and 708 cm^{-1}. NMR, δ 1.21 (d, J=7 Hz, 6H), 2.18 (s, 3H), 2.85 (m, J=7 Hz, 1H), and 6.7—7.2 (m, 4H).

*Irradiation of Mesityl Oxide (**93**) in Alcohols in the Presence of Uranyl Chloride.* Solutions of **93** (0.1 g) and uranyl chloride (0.04 g) in the following alcohols (10 ml) were irradiated in Pyrex tubes for 6 h. Subsequent work-ups afforded the following products.

In Ethanol: The irradiation product, which was assumed, on the basis of NMR analysis, to be a mixture of **109b** and **110b** was directly oxidized with CrO_3–pyridine–HCl in the way described above. The products were **95** (13% from **93**) and **120** (trace). The spectroscopic data of **120** were identical with those previously reported.[54]

In 2-Propanol: The products were **95** and **121**. The compound **121** was identical with the one reported previously.[55]

*Irradiation of Dimethyl Maleate (**26**) in Alcohols in the Presence of Uranyl Chloride.* Solutions of **26** (1.0 g) and uranyl chloride (0.24 g) in the following alcohols were irradiated in Pyrex tubes for 1 h, and then treated as follows.

In Ethanol: The oil remaining after the work-up was distilled under reduced pressure to give an oil (bp 106—108 °C (4 mmHg), 0.79 g). Although this oil (Oil A) was assumed to be a mixture of stereoisomeric esters **122a** and lactones **123a** *(vide infra)*, it gave *cis*- and *trans*-lactones **123a** (54: 46) (bp 99—102 °C (5 mmHg)) when kept at 200 °C for 2 h. The stereochemistry of the lactones was assigned on the basis of the NMR spectrum by comparing it with those previously reported.[3b] By subtracting the spectra of the lactones from the NMR spectrum of Oil A, we assigned the structure of the γ-hydroxy esters **122a** to the rest of the components. Although the amount of *cis*-lactone exceeds that of the *trans*-isomer in Oil A, amounts became almost equal after the thermal cyclization. We concluded from this result that the major component of the hydroxy esters in Oil A is probably the *threo*-isomer. From the distinctive methyl signals in the NMR spectrum of Oil A, we estimated the yields of the components as follows: *threo*-**122a** (23%), *erythro*-**122a** (14%), *trans*-**123a** (6%), and *cis*-**123a** (13%).

We assigned the NMR signals for **122a** as follows: [δ 1.15 (d, J=7 Hz) for *threo* and 1.18 (d, J=7 Hz) for *erythro*] 3H, 2.6—3.3 (m, 3H), 3.58 (b, 1H, disappears by D_2O), 3.75 (s, 3H), 3.79 (s, 3H), and 4.0—4.3 (m, 1H).

In 2-Propanol: The oil remaining after the work-up was identified by means of NMR analysis as a mixture of **122b**, **123b**, and the starting material (**26**) (76: 11: 13). Further purification was not achieved, and so the spectroscopic data of **122b** were obtained by subtracting those of **123b** and **26** from the spectra of the mixture. **122b**: IR, 3525, 1740, and 1175 cm^{-1}. NMR, δ 1.16 (s, 3H), 1.20 (s, 3H), 2.6—2.8 (bs, 3H), 3.18 (bs, 1H, disappears by D_2O), 3.63 (s, 3H), and 3.67 (s, 3H).

The distillation under reduced pressure induced the cyclization of **122b** into **123b**; the distillate (bp 108—110 °C (4 mmHg), 0.71 g) was a mixture of **122b**, **123b**, and **26** (9: 74: 17), as shown by NMR analysis. The spectroscopic data of the purified **123b** were identical with those previously reported.[3b,49]

*Irradiation of Mesityl Oxide (**93**) in Tetrahydrofuran in the Presence of Uranyl Chloride.* A solution of **93** (0.1 g) and uranyl chloride (0.03 g) in tetrahydrofuran (10 ml) was irradiated in a Pyrex tube for 4 h. A subsequent work-up afforded an oil which was almost pure **128**. MS, *m/e* 113 (M—CH_2-COMe), 98, 86, 72 (base peak), and 71. IR (neat), 2950, 2860, 1700, 1355, and 1060 cm^{-1}. NMR, δ 0.89 (s, 3H), 0.98 (s, 3H), 1.4—2.0 (m, 4H), 2.05 (s, 3H), 2.18 and 2.40

(ABq, J=14 Hz, 2H), and 3.4—3.8 (m, 3H).

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References

1) Preliminary reports; a) T. Sato, O. Ito, and M. Miyahara, *Chem. Lett.*, **1976**, 295; b) T. Sato and S. Yoshiie, *ibid.*, 415.

2) T. Sato, G. Izumi, and T. Imamura, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 788; *Tetrahedron Lett.*, **1975**, 2191.

3) a) M. Tokuda, Y. Yokoyama, T. Taguchi, A. Suzuki, and M. Itoh, *J. Org. Chem.*, **37**, 1859 (1972); b) S. Mejeti, *J. Org. Chem.*, **37**, 2914 (1972).

4) S. A. M. T. Hussain, W. D. Ollis, C. Smith, and J. F. Stoddart, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1480.

5) U. S. Patent 3577455; *Chem. Abstr.*, **75**, 197145 (1971).

6) P. Cerutti and H. Schmid, *Helv. Chim. Acta*, **45**, 1992 (1962).

7) P. Cerutti and H. Schmid, *Helv. Chim. Acta*, **47**, 203 (1964).

8) T. S. Cantrell, *J. Am. Chem. Soc.*, **94**, 5929 (1972).

9) N. C. Yang, B. Kim, W. Chiang, and T. Hamada, *J. Chem. Soc., Chem. Commun.*, **1976**, 729.

10) T. M. Patrick, Jr., *J. Org. Chem.*, **17**, 1269 (1952).

11) J. E. Whiting and J. T. Edward, *Can. J. Chem.*, **49**, 3799 (1971).

12) We believe that the chemical shift of the methylene proton in the *meso*-isomer, which has been reported[7] as τ 5.90, should be τ 6.90.

13) G. Balogh and F. C. DeSchryver, *Tetrahedron Lett.*, **1969**, 1371.

14) N. C. Yang and D-M. Thap, *Tetrahedron Lett.*, **1965**, 3671.

15) We designated the isomer leading to the *trans*-lactone as *threo*.

16) B. Fraser-Reid, D. R. Hicks, D. L. Walker, D. E. Iley, M. B. Yunker, S. Y-K. Tam, and R. C. Anderson, *Tetrahedron Lett.*, **1975**, 297; A, Guzmán and J. M. Muchowski, *ibid.*, 2053.

17) Z. Yoshida and M. Kimura, *Tetrahedron*, **31**, 221 (1975).

18) R. Matsushima, T. Kishimoto, and M. Suzuki, *Bull. Chem. Soc. Jpn.* **48**, 3028 (1975).

19) N. W. Alcock, N. Herron, T. J. Kemp, and C. W. Shoppee, *J. Chem. Soc., Chem. Commun.*, **1975**, 785.

20) T. Sato, K. Tamura, K. Maruyama, O. Ogawa, and T. Imamura, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 779.

21) J. D. Hefley, D. M. Mathews, and E. S. Amis, *Inorg. Synth.*, **7**, 146 (1963).

22) W. S. Rapson and R. Robinson, *J. Chem. Soc.*, **1935**, 1285.

23) W. W. Rinne, H. R. Deutsch, M. I. Bowman, and I. B. Joffe, *J. Am. Chem. Soc.*, **72**, 5759 (1950).

24) W. F. Gannon and H. O. House, *Org. Synth.*, Coll. Vol. V, 294 (1973).

25) E. L. Eliel and C. Lukach, *J. Am. Chem. Soc.*, **79**, 5986 (1957).

26) H. E. Zimmerman, P. Klackett, D. F. Juers, J. M. McCall, and B. Schröder, *J. Am. Chem. Soc.*, **93**, 3653 (1971).

27) O. E. Curtis, Jr., J. M. Sandri, R. E. Crocker, and H. Hart, *Org. Synth.*, Coll. Vol. IV, 278 (1963).

28) G. W. Cannon, R. C. Ellis, and J. R. Leal, *Org. Synth.*, Coll. Vol. IV, 597 (1963).

29) G. Stork, A. Brizzolara, H. Landesman, J. Szmuskovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

30) E. H. Man, F. W. Swamer, and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 901 (1951).

31) A. W. Johnson, E. Markham, and R. Price, *Org. Synth.*, Coll. Vol. V, 785 (1973).

32) R. B. Moffett, *Org. Synth.*, Coll. Vol. IV, 605 (1963).

33) T. F. West, *J. Soc. Chem. Ind.*, **61**, 158 (1942).

34) T. Cuvigny, H. Normant, and P. Hullot, *Bull. Chim. Soc. Fr.* **1970**, 3876.

35) E. P. Kyba, *Org. Prep. Proced.*, **2**, 149 (1970); *Chem. Abstr.*, **73**, 109422x (1970).

36) S. Natelson and S. P. Gotteried, *J. Am. Chem. Soc.*, **61**, 1001 (1939).

37) *Cf.* I. A. Favorskaya and L. V. Fedorcova, *Zh. Obshch. Khim.*, **23**, 47 (1953); *Chem. Abstr.* **48**, 610i (1954).

38) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, **1975**, 2647.

39) *Cf.* H. Schwarz, F. Bohlmann, and W. Volreander, *Org. Mass Spectrum*, **7**, 1005 (1973); *Chem. Abstr.*, **79**, 91180d (1973).

40) "The Aldrich Library of NMR Spectra," Vol. VI, Aldrich Chemical Company, Inc, Milwaukee, Wis. (1974), p. 87D.

41) Ref. 40, p. 88A.

42) Ref. 40, Vol. IV, p. 10D.

43) *Cf.* J. Debrauwere and M. Verzele, *Bull. Soc. Chim. Belg.*, **84**, 167 (1975); *Chem. Abstr.*, **83**, 25073c (1975).

44) S. Tanimoto, A. Kita, M. Okano, and R. Oda, *Yuki-gosei Kagaku Kyokaishi*, **27**, 444 (1969).

45) D. R. Marshall and T. R. Roberts, *J. Chem. Soc.*, **1971** (B), 797.

46) K. B. Wiberg and T. W. Hutton, *J. Am. Chem. Soc.*, **76**, 5367 (1954).

47) S. M. Davtyan, G. L. Papayan, and S. N. Asratyan, *Arm. Khim. Zh.*, **23**, 251 (1970); *Chem. Abstr.*, **73**, 25030e (1970).

48) G. F. Hennion and W. S. Murray, *J. Am. Chem. Soc.*, **64**, 1220 (1942).

49) K. Fukunichi, Y. Inoue, Y. Kishimoto, and F. Mashio, *J. Org. Chem.*, **40**, 628 (1975).

50) J. Falbe, N. Huppes, and F. Karte, *Chem. Ber.*, **97**, 863 (1964).

51) H. C. Brown and K. A. Keblys, *J. Org. Chem.*, **31**, 485 (1966).

52) P. H. Begemann, V. Lamberti, and W. T. Weller, *Rec. Trav. Chim. Pays-Bas*, **86**, 1335 (1967).

53) F. E. Condon, *J. Am. Chem. Soc.*, **71**, 3544 (1949).

54) D. A. Frost and G. A. Morrison, *J. Chem. Soc. Perkin Trans. 1*, **1973**, 2159.

55) T. Sato, T. Inoue, and K. Yamamoto, *Bull. Chem. Soc. Jpn*, **45**, 1176 (1972).

56) R. Lee, A. Kimura, and S. Isoe, Abstr. No. 1U28, 36th National Meeting of the Chemical Society of Japan, Osaka, April 1977; private communication from Prof. Isoe.