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Photoreactions of Cyclic Benzylidene Acetals with Ketones in the Presence and Absence of Dissolved Oxygen

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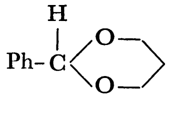
Photoreactions of 2-phenyl-1,3-dioxane (1) and 4,6-*O*-benzylidene-1,2,3-tri-*O*-acetylglucopyranose (**10**) in the presence of benzophenone, acetophenone, or acetone have been studied in both deoxygenated and aerated benzene solutions at room temperature. Photolysis of **1** with ketone in deoxygenated solution gave a dimeric product of **1** (**8**), cross adduct, and pinacol, while in aerated solution an oxidative ring cleavage product, *i.e.*, trimethylene glycol monobenzoate (**9**), was obtained instead of **8**, besides smaller amounts of pinacol and cross adduct. The yields of pinacol and cross adduct decreased with the change in ketone in the order benzophenone>acetophenone>acetone, while the yield of **8** or **9** was in the reverse order. Photolysis of **10** with ketone led to results parallel to those of **1**: photolysis under nitrogen atomosphere gave pinacol, cross adduct, and a dimeric product of **10** (**14**), while under bubbling air 4-*O*-monobenzoate and 6-*O*-monobenzoate derivatives of **10** were obtained instead of **14**, besides pinacol and cross adduct. The effects of temperature, oxygen, and structure on the course of the reaction, to produce dimeric or ring opening products, have been discussed.

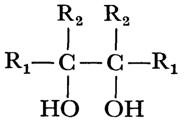
Recently photoreactions of carbohydrate derivatives have been extensively studied.[1] Photochemical hydrogen abstraction from 2-alkyl-1,3-dioxanes[2] or from benzylidene derivatives of L-ribose[3] with acetone gives ring opening (β-cleavage) products, while photolysis of *o*-nitrobenzylidene derivatives of glucose gives oxidative ring opening products *via* intramolecular hydrogen abstraction followed by oxidation of the intermediate radicals.[4] Photoreactions of 2-aryl-1,3-dioxanes with ketone seem to have been little studied, though hydrogen abstraction from 2-phenyl-1,3-dioxanes by thermally generated *t*-butoxyl radicals[5] or NBS[6] produces ring opening products. In this work studies on the photoreactions of 2-phenyl-1,3-dioxane and its derivative of triacetylglucopyranose with ketone have been carried out, showing some different features from those referred to above.

Results

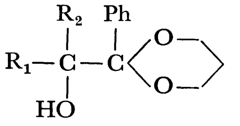
Photolysis of 2-Phenyl-1,3-dioxane with Ketone. Irradiation of a benzene solution of 2-phenyl-1,3-dioxane (**1**) in the presence of benzophenone, acetophenone, or acetone, at 15 °C under oxygen-free nitrogen atomosphere, gave the corresponding pinacol (**2**, **3**, or **4**, respectively), cross adduct (**5**, **6**, or **7**, respectively), and a dimer (**8**).



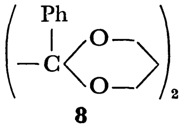
1



Pinacol



Cross adduct

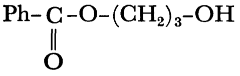


8

2: $R_1=R_2=Ph$
3; $R_1=Ph$, $R_2=Me$
4: $R_1=R_2=Me$

5: $R_1=R_2=Ph$
6: $R_1=Ph$, $R_2=Me$
7: $R_1=R_2=Me$

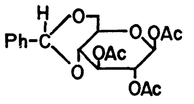
On the other hand, photolysis of the same solution under bubbling air gave trimethyleneglycol monobenzoate (**9**) instead of the dimer **8**, besides pinacol and cross adduct.



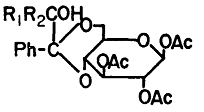
$Ph-C(=O)-O-(CH_2)_3-OH$ **9**

The results are summarized in Table 1. We see a significant change in the product distribution: the yields of pinacol and cross adduct decrease with the change in the ketone in the order benzophenone> acetophenone>acetone, while the yield of **8** or **9** is in the reverse order.

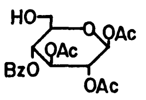
Photolysis of 4,6-O-Benzylidene-1,2,4-tri-O-acetyl-β-D-glucopyranose with Ketone. Irradiation of benzene solution of 4,6-*O*-benzylidene-1,2,3-tri-*O*-acetyl-β-D-glucopyranose (**10**) in the presence of benzophenone, acetophenone, or acetone, at 15 °C under oxygen-free nitrogen atomosphere, gave the corresponding pinacol (**2**, **3**, or **4**, respectively), cross adduct (**11**, **12**, or **13**, respectively), and a dimer (**14**). Photolysis of the same solution as above under bubbling air gave 4- and 6-*O*-benzoyl-1,2,3-tri-*O*-acetylglucopyranose (**15**) and (**16**), instead of the dimer **14**, besides pinacol and cross adduct. The results are summarized in Table 2.



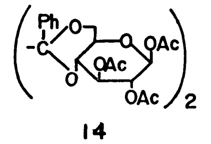
10



Cross adduct

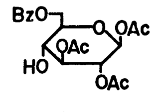


15



14

	R_1	R_2
11	Ph	Ph
12	Ph	Me
13	Me	Me



16

Quantum Yields for Hydrogen Abstraction. In order to see the structural factors affecting the efficiency for the abstraction of tertiary hydrogen atoms by excited state ketones, quantum yields for the hydrogen abstraction process have been measured for various substrate-ketone systems. On the basis of the following scheme

$$\begin{tikzcd} K \arrow[r, "h\nu"] & {}^1K^* \arrow[r, "\phi_{st}\fallingdotseq 1"] & {}^3K^* \arrow[r, "k_d"] \arrow[d, "k_r", "RH"'] & K + \text{heat or } h\nu' \\ & & KH + R\cdot \rightarrow\rightarrow \text{products} & \end{tikzcd}$$

assumed for the photoreaction of a ketone (K) with a hydrogen donor (RH), the rate expression is given by

Table 1. Yields of the products by the photolysis of **1** (0.1 M) with ketone

Conditions		Products and yields[a)]				Recovery of **1**, %
Atmosphere	Ketone, M	Pinacol, %	Adduct, %	**8**, %	**9**, %	
N_2	Benzophenone, 0.1	**2**, 28	**5**, 36	9.5	0	trace
N_2	Acetophenone, 0.1	**3**, 18	**6**, 30	13	0	20[b)]
N_2	Acetone, 1.3	**4**, trace	**7**, 17	17	0	45
Air	Benzophenone, 0.1	**2**, 19	**5**, 27	0	35	10[c)]
Air	Acetone, 1.3	**4**, 0	**7**, 5	0	70	40

a) Based on the consumed amount of **1**. b) Recovered yield of acetophenone was 19%. c) Recovered yield of benzophenone was 48%.

Table 2. Yields of the products of the photolysis of **10** (0.05 M) with ketone

Conditions		Products and yields[a)]					Recovery of **10**, %
Atomosphere	Ketone, M	Pinacol, %	Adduct, %	**14**, %	**15**, %	**16**, %	
N_2	Benzophenone, 0.05	**2**, 26	**11**, 38	trace	0	0	15[b)]
N_2	Acetophenone, 0.05	**3**, 16	**12**, 33	7	0	0	20[c)]
N_2	Acetone, 1.3	**4**, trace	**13**, 23	9	0	0	46
Air	Benzophenone, 0.05	**2**, 19	**11**, 17	0	27	19	23[d)]
Air	Acetone, 1.3	**4**, 0	**13**, trace	0	41	23	37

a) Based on the consumed amount of **10**. b) Recovered yield of benzophenone was 10%. c) Recovered yield of acetophenone was 17%. d) Recovered yield of benzophenone was 70%.

Table 3. Rate parameters for the abstraction of tertiary hydrogen atoms by excited state ketones[a)]

Substrate	Ketone	ϕ	k_d/k_r, M
1	Benzophenone	0.64	0.056
1	Acetophenone	0.37	0.17
1	Acetone	0.11	0.77
$(EtO)_2CHPh$	Benzophenone	0.52	0.093
Ph_2CHOH	Benzophenone	0.67[b)]	0.05
Me_2CHOH	Benzophenone	0.71[c)]	0.18
Me_2CHPh	Benzophenone	0.30	0.23

a) Quantum yields at initial substrate concentration of 0.1 M. Initial concentrations of benzophenone and acetophenone were 0.1 M while that of acetone was 1.3 M. b) Ref. 7, p. 3. c) Data from S. G. Cohen, *Tetrahedron Lett.*, **1968** 4823.

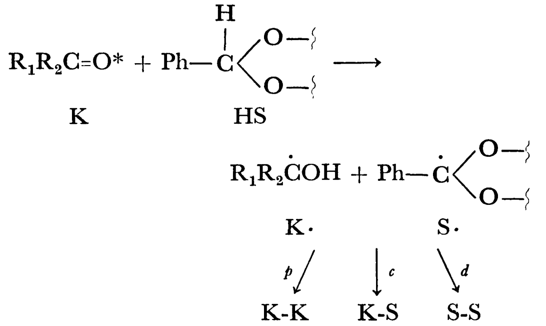
$1/\phi = 1 + k_d/k_r[\text{RH}]$,[7)] where, ϕ is the quantum yield of disappearance of RH or K. If the equation is multiplied by the quantum yield ϕ_s of the disappearance of K, known for a standard system such as ketone–benzhydrol,[8)] we have

$$\frac{\phi_s}{\phi} = \phi_s + \frac{k_d\phi_s}{k_r[\text{RH}]}$$

Thus, ϕ and k_d/k_r can be obtained from the slope and intercept of a plot of the relative disappearance ratio *vs.* $1/[\text{RH}]$, using a value of $\phi_s = 0.68$ for 0.1 M benzophenone and 0.1 M benzhydrol.[8)] The results are given in Table 3.

Discussion

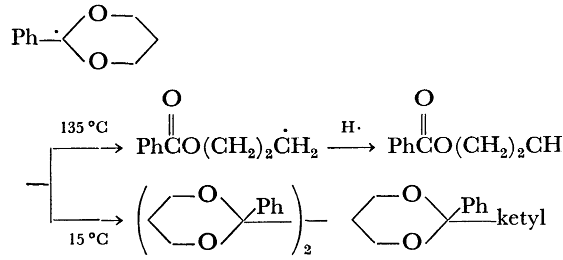
Effects of Temperature and the Substrate Structure on the Course of the Reaction. The variation in the product yields with the change in ketone (Tables 1 and 2) might be related to the relative stability of ketyl radicals (K·). The yields of pinacols (K-K) and cross adducts (S-K) would decrease in the decreasing order of relative stability of ketyl radicals; the yield of the dimer (S-S), whose formation process *d* being competitive with the process *c*, would increase.



Acetone ketyl radical would rapidly react with solvent, though no further investigation was made on the products. The product ratio of the photolysis of **1** with acetophenone, 3 : 6 : 8=1 : 2.3 : 1.4 (Table 1), is close to the statistical ratio 1 : 2 : 1 which is inferred for the two radicals with similar stability, suggesting that S· is as stable as the acetophenone ketyl radical.

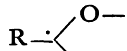
The reaction of S· shows a remarkable temperature dependence: at 15 °C S· (produced by hydrogen atom abstraction by excited state acetone) gives a dimer and cross adduct without ring opening (Table 1), while at 135 °C S· (produced by thermal hydrogen atom abstraction with *t*-butoxyl radical) gives a ring opening product.[5)]

At low temperature, S· is stable enough to undergo collisional encounters with other radicals, resulting in dimerization and cross coupling reactions which are assumed to involve no significant activation processes and to be highly exothermic. At high temperature,



S· is somewhat activated or destabilized and unimolecular ring opening (*β*-cleavage), assumed to involve more or less activation process, would occur before bimolecular encounter of radicals.

A significant structural effect is observed on the features of the following intermediate radical:



(R = alkyl or phenyl)

Upon irradiation in the presence of acetone at room temperature 2-alkyl-1,3-dioxane undergoes ring opening to give $RC(=O)O(CH_2)_2CH_3$ as the main product,[2] in contrast with the present results of 2-phenyl-1,3-dioxane (Table 1). The difference might be correlated to the relative stability of the intermediate radicals: the radical with R = alkyl is not so stabilized as that with R = phenyl whose resonance stabilization energy due to the benzyl group is *ca.* 18 kcal/mol.[9] Thus, the ring opening process of 2-phenyl-1,3-dioxane is expected to be much more endothermic than that of 2-alkyl-1,3-dioxane.

The product yields of the photolysis of **10** with benzophenone, acetophenone, or acetone are almost the same as those of the photolysis of **1** under similar conditions. The yields of the dimer **14** are lower and those of the cross adducts are slightly higher in Table 2 than the yields of the corresponding products in Table 1. This may reflect a larger steric hindrance of the intermediate radical derived from **10** as compared to that from **1**. Mutual coupling of bulky radicals to form **14** would sterically be less favorable as compared to the cross coupling with less bulky benzophenone ketyl radical.

Effects of the Dissolved Oxygen. The yields of pinacols, cross adducts and dimers decrease in the presence of oxygen. Oxidative ring opening products (benzoates) are formed in a significant yield (Tables 1 and 2). This shows a high reactivity of oxygen with the intermediate radicals.[3,4]

The fact that the benzoate derivatives are formed by the photoreaction in the presence of oxygen whereas they are not formed under purified nitrogen atmosphere, indicates that the source of oxygen (necessary for the formation of the benzoates) is the dissolved oxygen. It is likely that the source of oxygen required for the formation of methyl-2(or 3)-*O*-benzoyl-*β*-D-ribofuranoside in acetone-sensitized photolysis of methyl-2,3-*O*-benzylidene-*β*-D-ribofuranoside under nitrogen (commercial nitrogen without further purification[3]), is the small amount of oxygen which might be contained in the commercial nitrogen.

Since the yields of the benzoate derivatives relative to those of the cross adducts or dimers depend on the concentration of the dissolved oxygen,[11] it seems that the formation of the benzoate derivatives takes place through the reaction of the radical S· with the dissolved oxygen and that this process is competitive with processes *c* and *d*.

When the consumption of **1** is 90%, that of benzophenone is only 52%, upon irradiation of an air-saturated benzene solution containing equimolar amount of **1** and benzophenone. The discrepancy in the consumption rates of **1** and benzophenone might be related to the reformation of benzophenone by the reaction of the benzophenone ketyl radical with the dissolved oxygen, according to the report by Pitts *et al.*:[12]

$$Ph_2\dot{C}OH + O_2 \longrightarrow Ph_2C{=}O + HOO\cdot$$

$$HOO\cdot + RH \text{ (substrate or solvent)} \longrightarrow H_2O_2 + R\cdot$$

However, the mechanism for the formation of the benzoate derivatives, *e.g.*, as to whether or not the reaction proceeds through radical chain process, is not clarified as yet. The radical chain mechanism does not seem to be supported by the apparent rate; the photoreaction in the presence of the dissolved oxygen seems to proceed less efficiently than that under nitrogen atmosphere, though the quantum yields for the photoreaction in the presence of the dissolved oxygen have not been measured.

Structural Effects on the Rates of Hydrogen Abstraction. We see a significant change in ϕ (Table 3) with the change in structure of the substrate or the ketone. The lowest triplet lifetimes (τ_T) of acetone, acetophenone, and benzophenone in benzene at room temperature are 0.94, 3.5, and 12 μs, respectively.[13] The results in the first three runs in Table 3 show that ϕ and k_d/k_r are closely related to τ_T, k_r/k_d being nearly proportional to τ_T. Thus, the efficiency of the hydrogen abstraction from the substrate **1** by different ketones is mainly controlled by the lowest triplet lifetimes of the ketones.

Since the bond dissociation energies of the benzylic hydrogen atoms of **1** and $(EtO)_2CHPh$ are assumed to be similar, the slightly low photoreactivity of $(EtO)_2CHPh$ as compared to that of **1** may be attributed to the steric hindrance due to the free rotation of the two ethoxyl groups in $(EtO)_2CHPh$. The intermediate radical $Ph_2\dot{C}OH$ is expected to be stabilized to a greater extent by the two phenyl groups as compared to $Me_2\dot{C}HO$. Nevertheless the efficiency for the hydrogen abstraction of Ph_2CHOH is not higher than that of Me_2CHOH. This may partly be due to a saturation effect (selectivity will be poor when hydrogen abstraction occurs on highly reactive substrates), as well as the steric hindrance.

Experimental

Materials. 2-Phenyl-1,3-dioxane[5] and 4,6-*O*-benzylidene-1,2,3-tri-*O*-acetyl-*β*-D-glucopyranose[14,15] were prepared according to methods in literature. Guaranteed benzophenone, acetophenone, and acetone (Wako Chemicals) were used.

Photolysis of 2-Phenyl-1,3-dioxane (1) with Benzophenone. After deoxygenation with purified nitrogen current for 1 h, a 125 ml benzene solution containing **1** (0.1 M) and benzophenone (0.1 M) was irradiated at 15 °C under purified nitrogen atmosphere with a 100 W high pressure mercury lamp for 5 h. The photolyzed solution was condensed and chromatographed over silica gel to give **2** (1.25 g), **5** (1.59 g) and **8** (0.39 g). **2** gave mp, NMR and IR spectra identical with those of authentic benzpinacol. **5**: colorless crystal, mp 189—190 °C; IR: 1580, 3520 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$): δ 1.0—1.4 (m, 1H, $\mathrm{H_{5e}}$), 1.9—2.7 (m, 1H, $\mathrm{H_{5a}}$), 3.12 (s, 1H, OH), 3.5—4.1 (m, 4H, $\mathrm{H_4H_6}$), 6.8—7.7 (m, 15H, phenyl). Found: C, 79.25; H, 6.47%. Calcd for $\mathrm{C_{13}H_{18}O_3}$: C, 79.74; H, 6.40%. **8**: colorless prism, mp 235—236.5 °C; IR: 2850, 2950 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$): δ 0.8—1.3 (m, 2H, $\mathrm{H_{5e}H_{5e}'}$), 1.5—2.3 (m, 2H, $\mathrm{H_{5a}H_{5a}'}$), 3.0—3.4 (m, 8H, $\mathrm{H_4H_4'H_6H_6'}$), 7.1—7.3 (m, 10H, phenyl). Found: C, 73.68; H, 6.95%. Calcd for $\mathrm{C_{20}H_{22}O_4}$: C, 73.60; H, 6.79%. Upon irradiation under bubbling air for 7.5 h, a 125 ml solution of the same as that above gave **9** (0.71 g), **2** (0.21 g) and **5** (1.06 g), besides recovered **1** (0.20 g) and benzophenone (1.18 g). **9** showed IR and NMR spectra identical with those of authentic trimethyleneglycol monobenzoate.

*Photolysis of 2-Phenyl-1,3-dioxane (**1**) with Acetophenone.* A 125 ml benzene solution containing **1** (0.1 M) and acetophenone (0.1 M) was irradiated in a similar way for 6 h under nitrogen atmosphere. Separation of the photolyzed solution by column chromatography over silica gel gave **3** (0.45 g), **6** (0.84 g), **8** (0.41 g), besides recovered **1** (0.41 g) and acetophenone (0.27 g). **3**: colorless prism, mp 121—122.5 °C (lit, 123—124 °C)[16]; IR: 1600, 2960, 3550 $\mathrm{cm^{-1}}$: NMR ($\mathrm{CDCl_3}$): δ 1.43 (s, 6H, Me), 2.72 (s, 2H, OH), 7.0—7.3 (m, 10H, phenyl). **6**: mp 114—116 °C; IR: 1590, 2850, 2950, 3560 $\mathrm{cm^{-1}}$; NMR: δ 0.84—1.4 (m, 1H, $\mathrm{H_{5e}}$), 1.63 (s, 3H, Me), 1.8—2.5 (m, 1H, $\mathrm{H_{5a}}$), 2.96 (broad s, 1H, OH), 3.4—4.0 (m, 4H, $\mathrm{H_4H_6}$), 6.8—7.3 (m, 10H, phenyl). Found: C, 76.14; H, 7.22%. Calcd for $\mathrm{C_{18}H_{20}O_3}$: C, 76.03; H, 7.09%.

*Photolysis of 2-Phenyl-1,3-dioxane (**1**) with Acetone.* A 125 ml benzene solution containing **1** (0.1 M) and acetone (1.3 M), after previous deoxygenation, was irradiated at 15 °C under purified nitrogen atmosphere with a 100 W high pressure mercury lamp for 20 h. Separation of the photolyzed solution by column chromatography over silica gel gave **7** (0.26 g), **8** (0.38 g) and **4** (a trace), besides recovered **1** (0.93 g). **7**: mp 90.5—92 °C; IR: 2900, 3550 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$): δ 1.10 (s, 6H, Me), 1.0—1.4 (m, 1H, $\mathrm{H_{5e}}$), 1.6—2.4 (m, 1H, $\mathrm{H_{5a}}$), 2.48 (s, 1H, OH), 3.4—4.0 (m, 4H, $\mathrm{H_4H_6}$), 7.3—7.5 (m, 5H, phenyl). Found: C, 70.71; H, 8.42%. Calcd for $\mathrm{C_{13}H_{18}O_3}$: C, 70.24; H, 8.16%. Upon irradiation under bubbling air for 30 h, 125 ml of the same solution as that above gave **7** (0.09 g), and **9** (0.95 g), besides recovered **1** (0.82 g).

*Photolysis of 3,6-O-Benzylidene-1,2,3-tri-O-acetyl-β-D-glucopyranose (**10**) with Benzophenone.* A 100 ml benzene solution containing **10** (0.05 M) and benzophenone (0.05 M) was deoxygenated with purified nitrogen current, and then irradiated at 15 °C under purified nitrogen atmosphere for 15 h. Separation of the photolyzed solution by column chromatography over silica gel gave **2** (0.43 g), **11** (0.93 g) and **14** (a trace), besides recovered **10** (0.30 g) and benzophenone (0.09 g). **11**: mp 235—236.5 °C; IR: 1750, 3520 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$): δ 1.99, 2.06 (2s, 9H, AcO), 3.05 (s, 1H, OH), 3.3—4.3 (m, 4H), 4.8—5.6 (m, 2H, $\mathrm{H_2H_3}$), 5.72 (d, 1H, J=7.7 Hz, $\mathrm{H_1}$), 6.7—7.9 (m, 15H, phenyl). Found: C, 66.57; H, 5.60%. Calcd for $\mathrm{C_{32}H_{32}O_{10}}$: C, 66.66; H, 5.59%. Upon irradiation under bubbling air for 15 h, 100 ml of the same solution as that above gave **2** (0.10 g), **15** (0.43 g) and **16** (0.30 g), besides recovered **10** (0.45 g) and benzophenone (0.64 g). **15**: mp 152.5—153.5 °C; IR: 1708, 1740, 3550 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$): δ 1.90, 2.00, 1.10 (3s, 9H, AcO), 2.6 (broad s, 1H, OH), 3.4—4.0 (m, 3H, $\mathrm{H_5H_6}$), 5.0—5.6 (m, 3H, $\mathrm{H_2H_3H_4}$), 5.80 (d, 1H, J_{12}=7.5 Hz, 1H), 7.8—8.1, 7.8—8.2 (m, 5H, phenyl). Found: C, 55.82; H, 5.48%. Calcd for $\mathrm{C_{19}H_{22}O_{10}}$: C, 55.61; H, 5.40%. **16** showed mp, IR and NMR spectra identical with those of an authentic sample of 6-*O*-benzoyl-1,2,3-tri-*O*-acetyl-*β*-D-glucopyranose which was prepared separately.

*Photolysis of 4,6-O-Benzylidene-1,2,3-tri-O-acetyl-β-D-glucopyraanose (**10**) with Acetophenone.* A 100 ml benzene solution containing **10** (0.05 M) and acetophenone (0.05 M) was deoxygenated with purified nitrogen current for 1 h, and then irradiated at 15 °C under purified nitrogen atmosphere for 30 h. Separation of the photolyzed solution by column chromatography over silica gel gave **3** (0.16 g), **12** (0.68 g) and **14** (0,68 g), besides recovered **10** (0.39 g) and acetophenone (0.10 g). **12**: mp 209.5—210.5 °C; IR: 1740, 3510 $\mathrm{cm^{-1}}$, NMR ($\mathrm{CDCl_3}$): δ 1.72 (s, 3H, Me), 1.99, 2.09 (2s, 9H, AcO), 2.51 (s, 1H, OH), 3.4—3.8 (m, 3H, $\mathrm{H_5H_6}$), 4.0—4.3 (m, 1H, $\mathrm{H_4}$), 4.8—5.5 (m, 2H, $\mathrm{H_2H_3}$), 5.71 (d, 1H, J_{12}=7.7 Hz, $\mathrm{H_1}$), 7.0—7.4 (m, 10H). Found: C, 58.18; H, 5.68%. Calcd for $\mathrm{C_{38}H_{42}O_8}$: C, 58.01; H, 5.38%.

*Photolysis of 4,6-O-Benzylidene-1,2,3-tri-O-acetyl-β-D-glucopyranose (**10**) with Acetone.* A 100 ml benzene solution containing **10** (0.05 M) and acetone (1.3 M) was deoxygenated with purified nitrogen for 1 h, and then irradiated at 16 °C under nitrogen atomosphere for 60 h. Separation of the photolyzed solution by column chromatography over silica gel gave **4** (a trace), **13** (0.28 g) and **14** (0.19 g), besides recovered **10** (0.91 g). **13**: mp 183—184.5 °C; IR: 1740, 3500 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$): δ 1.02 1.17 (2s, 6H, Me), 2.00—2.10 (2s, 9H, AcO), 2.00—2.15 (s, 1H, OH), 3.4—3.8 (m, 3H, $\mathrm{H_5H_6}$), 4.0—4.3 (m, 1H, $\mathrm{H_4}$), 4.7—5.3 (m, 2H, $\mathrm{H_2H_3}$), 5.52 (d, 1H, J_{12}=7.7 Hz, $\mathrm{H_1}$), 7.3—7.4 (m, 5H, phenyl). Found: C, 58.85; H, 6.44%. Calcd for $\mathrm{C_{22}H_{18}O_{10}}$: C, 58.40; H, 6.24%. Upon irradiation under bubbling air, 100 ml of the same solution as that above gave **12** (a trace), **15** (0.53 g) and **16** (0.30 g), besides recovered **10** (0.72 g).

Quantum Yields. Quantum yields were estimated from the plot of relative disappearance ratio *vs.* the reciprocal concentration of **1**. Benzene solutions containing ketone and various concentrations of **1** in identical pyrex tubes were irradiated with a merry-go-round irradiation apparatus with a 400 W high pressure mercury lamp. Initial concentrations of **1** were 0.08, 0.10, 0.15, 0.20 and 0.25 M, while that of benzophenone or acetophenone was 0.1 M and acetone 1.3 M. Each solution was deoxygenated before irradiation. The irradiation time was 15 min for the **1**-benzophenone system, 40 min for the **1**-acetophenone system, and 7 h for the **1**-acetone system: the extent of reaction for each system was nearly 15%. The colorimetric method was used to determine the disappearance of benzophenone or acetophenone, while for the **1**-acetone system NMR signal intensity at δ=5.4 of **1** was measured to determine the disappearance of **1**.

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