The Convenient Syntheses of 4-(2,3-Dihydroxypropoxy)-4'-Substitued Dibenzoylmethane Derivatives as Hydrophilic Ultraviolet Absorbing Agents

Yoshifumi Yuasa, Akiko Horizoe

Kasai Chemical Laboratory

7-7-402 Akashicho, Hiratsuka, Kanagawa, 254-0042, Japan

Abstract

*New dibenzoylmethane derivatives **1a-e** having a glyceryloxy group as the hydrophilic nature have been synthesized by the condensation of 4-acetonidebenzoate **5** and 4-subustited acetophenone **6a-e** in the presence of $NaNH_2$, followed by acidic hydrolysis. These compounds **1a-e** have an excellent solubility in oily and water-soluble bases and are expected to be the extremely useful as UV absorbers in the UV-A region.*

Keywords — *UV absorber; UV-A region, Dibenzoylmethane derivative, Glyceryloxy group, Hydrophilic.*

I. INTRODUCTION

Ultraviolet absorbers have been conventionally used in many technical fields. For example, in the field of cosmetics, they are blended in various cosmetics for the purpose of protecting the skin[1)]. Ultraviolet rays are classified into UV-A, UV-B, and UV-C, depending on their wavelength range. Among them, ultraviolet rays in the UV-B range are known to cause skin damage such as acute erythema formation[1)]. The development of UV absorbers has been mostly directed to UV absorbers in the UV-B region. However, it has been found that UV rays in the UV-A region have the effect of enhancing pigmentation such as spots and freckles and skin damage caused by UV rays in the UV-B region. For example, various dibenzoylmethane derivatives **1** are known as substances that absorb UV rays in the UV-A region. Specifically, two benzene rings substituted with an alkoxy group, one substituted with an alkyl group, 4-*t*-butyl-4'-methoxydibenzoylmethane[2)] (**1**: R_1 = *t*-Bu, R_2 = Me, Parsol 1789) and analog dibenzoylmethanes are well known[3)]. However, these compounds are all hydrophobic, and when blended in cosmetics, they can be easily mixed with an oleaginous base, but are difficult to mix with a water-soluble base. Therefore, in order to increase the water solubility of these dibenzoylmethane derivatives, those containing a quarternary ammonium group or those an alkoxycarbonyl group have been developed[4,5)], whereas the benzophenone derivatives are known as substances that absorb UV-A and UV-B ultraviolet rays, and have two hydroxyl groups and a glyceryl ether group (glyceryloxy group) or a polyglyceryl ether group in each of the two benzene rings and are known as water-soluble UV absorbers[6)].

In order to improve the these problems of conventional hydrophobic ultraviolet absorbers, those having hydrophilic properties and have an ultraviolet absorption effect in the UV-A region have been developed, but there are only few compounds that can satisfy this requirement, and thus only parasol 1789 is used. The authors now report the dibenzoylmethane derivatives having a hydrophilic ultraviolet absorber agent in the UV-A region.

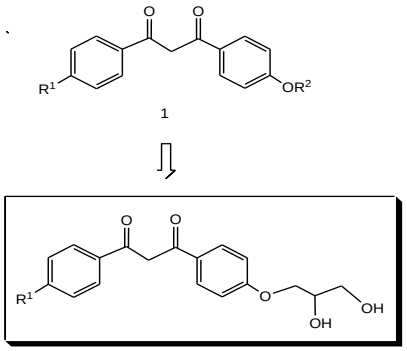
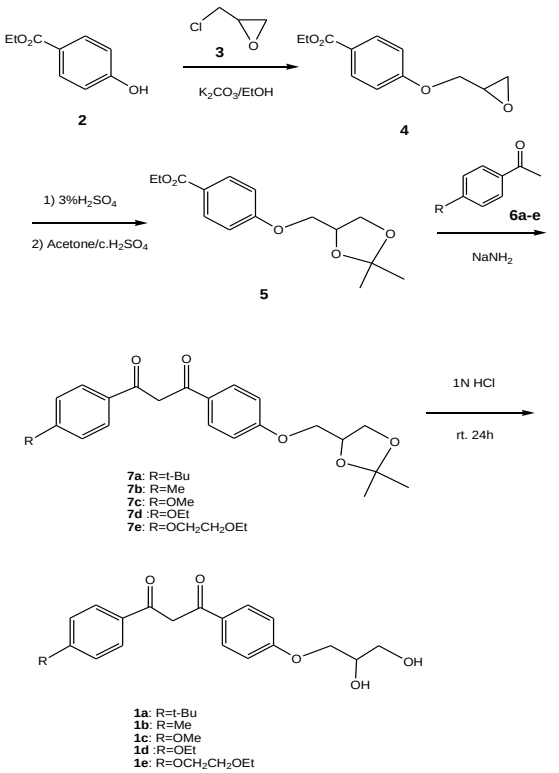


Fig. 1: The structure of dibenzoylmethane derivatives as UV-A absorber

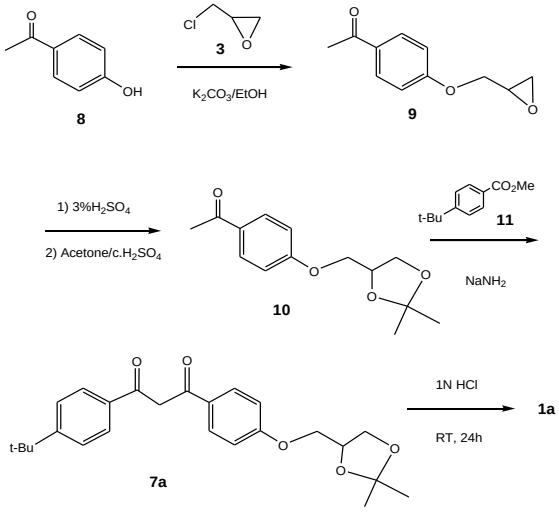
II. RESULTS AND DISCUSSION

Ethyl 4-hydroxybenzoate **2** was reacted with epichlorohydrin **3** in the presence of K_2CO_3 by heating to give 4-oxranylmethoxybenzoate **4** with a 70% yield. After cleaving the oxiran ring by 3% H_2SO_4 as a weak acid[7)], acetone/conc. H_2SO_4 was used to produce an acetonide **5**. The condensation of benzoates and acetophenones by a strong base is well known as the general synthetic method of dibenzoylmethanes[8)]. Thus, **5** and 4-substitued acetophenone **6** were condensed with $NaNH_2$ as a strong base to give dibenzoylmethanes **7a-e**. Furthermore, **7a-e** were hydrolyzed to afford **1a-e** having a glyceryloxy group (Scheme 1). These compounds **1a-e** are all new materials.



Scheme 1: Synthesis of **1a** from acetonide **5** and methyl 4-hydroxyabenzoate **6**

Also, another synthetic route was studied, thus 4'-hydroxyacetophenone **8** and epichlorohydrin **3** were reacted by using K_2CO_3 to afford 4-oxranaceto-phenone **9** and then hydrolyzed, followed by acetonidation to give **10**. The condensation of **7** and methyl 4-*t*-butylbenzoate **11** gave **7a** and hydrolyzed to afford **1a** in the same manner as Scheme 1 (shown in Scheme 2).



Scheme 2: Synthesis of **1a** from acetophenone **10** and methyl 4-*t*-butylbenzote **11**

The synthesized compounds **1a**-**1e** were examined for their UV absorption effect and solubility in a water-soluble base. Thus, **1a-e** and Parsol 1789 as the control were measured by dissolving in ethanol and measuring the maximum absorption wavelength (absorption maximum value, λmax; nm) of the UV absorption spectrum and the molecular extinction coefficient (ε) at the maximum absorption wavelength. The results are shown in Table 1.

Table 1: Maximal absorption of UV spectra and solubility

Compd.	UV spectra λmax(nm)	ε	Solubility for 50% EtOHaq. (mg/100g) at 25°C
1a	358	38,100	400
1b	362	41,300	600
1c	357	35,700	70
1d	363	42,500	90
1e	362	41,700	100
Parsol 1789	358	36,100	Insoluble

Therefore, the new compounds **1a**-**e** had a maximum absorption wavelength of around 360 nm and a molecular extinction coefficient equal to or greater than that of Parsol 1789. Moreover, it became clear that the solubility with respect to a 50% ethanol water mixed solution occurs whereas Parsol 1789 is not dissolved (Table 1).

III. MATERIALS AND METHOD

All reagents and solvents were obtained from commercial sources and used without further purification. The melting points were determined using a Yanagimoto micromelting apparatus and are uncorrected. The UV spectra were obtained using a Shimazu UV-260. The NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard using a Bruker AM-400 (400MHz) spectrometer. The (), chemical shifts are given in ppm. The mass spectra (electronic impact at 20eV) and high-resolution mass (HRMS) spectra were obtained using a Hitachi M-80A spectrometer.

Synthetic procedures

Ethyl 4-(oxoranylmethoxy)benzoate (**4**): In a 5-L glass vessel, ethyl 4-hydroxy benzoate **2** (500 g, 3.0 mol), K_2CO_3 (218 g, 1.58 mol), epichlorohydrin **3** (555 g, 6.0 mol) and EtOH (1.5 L) were added and the reaction mixture was stirred at 80 °C for 6h. After the solvent was recovered under reduced pressure, toluene (2.5 L) was added to the residue, then washed several times with water. The toluene layer was concentrated under reduced pressure and the crude product was distilled to give **4** (470 g, 70%) as an oil. Bp. 143°C/0.3 Torr, Mp. 47 - 49°C , ^{1}H-NMR ($CDCl_3$) 1.37 (t, *J* = 7.1Hz, 3H), 2.75 (dd, *J* = 2.6Hz, 4.9Hz, 1H), (m, 2H), 2.90 (dd, *J* = 4.2Hz, 4.9Hz, 1H),

3.35 (m, 1H), 3.96 (dd, *J* = 5.8Hz, 11.0Hz, 1H), 4.29 (dd, *J* = 2.9Hz, 11.0Hz, 1H), 4.34 (q, *J* = 7.1Hz, 2H), 6.93 (m, 2H), 7.99 (m, 2H). ^{13}C-NMR ($CDCl_3$) 14.33, 44.49, 49.85, 60.63, 68.81, 114.12, 123.44, 131.51, 162.06, 166.18. MS: 222 (M^+), 177, 138, 121, 93, 57, 29. Anal. calcd. for $C_{12}H_{14}O_2$: C 64.85, H 6.35; found: C 64.88, H 6.37.

Ethyl 4-[(2,2-dimethyl-1,3-dioxoran-4-yl)-methoxy]-benzoate (**5**): In a 5-L glass vessel, **4** (466 g, 2.1 mol), acetone (3 L) and a 3%H_2SO_4 aqueous solution (950 g) were added and the reaction mixture was stirred at 60°C for 4 hr. After the reaction mixture was neutralized by Na_2CO_3, it was washed with a saturated NaCl aqueous solution. The organic layer was separated, and the acetone was recovered. After toluene was added, the water was removed from the reaction residue and the residual salt was filtered. Acetone (1 L) and 98% H_2SO_4 (8 g) were added to the filtered solution and stirred overnight at room temperature. After the reaction mixture was neutralized by Na_2CO_3, the salts were filtered off. The residue was concentrated at reduced pressure, toluene (2 L) was added, then and washed with water. After the organic layer was concentrated, isopropyl ether (1.2 L) was added to afford **5** (429 g, 73%) as white crystals. Mp. 60 - 62°C, ^{1}H-NMR ($CDCl_3$) 1.38 (t, *J* = 7.1Hz, 3H), 1.41 (s, 3H), 1.47 (s, 3H), 3.91 (dd, *J* = 5.8Hz, 8.6Hz, 1H), 4.00 (dd, *J* = 5.8Hz, 9.6Hz, 1H), 4.10 (dd, *J* = 5.3Hz, 9.6Hz, 1H), 4.18 (dd, *J* = 2.1Hz, 8.6Hz, 1H), 4.35 (q, *J* = 7.1Hz, 2H), 4.49 (m, 1H), 6.94 (m, 2H), 7.99 (m, 2H). ^{13}C-NMR ($CDCl_3$) 14.34, 25.32, 26.75, 60.66, 66.70, 68.83, 73.84, 109.88, 114.09, 123.42, 131.53, 131.58, 162.18, 166.28. MS: 280 (M^+), 265, 235, 205, 121, 101, 59. Anal. calcd. for $C_{15}H_{20}O_5$: C 64.27, H 7.19; found: C 64.30, H 7.20.

General procedure of **7**

4-[(2,2-Dimethyl-1,3-dioxyran-4-yl)-methoxy]-4'-(1,1-Dimethylethyl)dibenzoylmethane (**7a**): In a 3-L glass vessel, $NaNH_2$ (31.2 g, 0.8 mol) and toluene (200 mL) were added. 5 (112 g, 0.4 mol) dissolved in toluene (100 mL) was dropwise added to the suspension for 30 min under N_2 gas. After stirring for 1 h, 4-t-butylacetophenone 6a (70.4 g, 0.4 mol) was added and stirred for 48 h. Toluene (500 mL) and dil. HCl (2 L) were added to the reaction mixture, the organic layer was extracted, washed and the solvent was recovered under reduced pressure. The residue was recrystallized from EtOH to give **7a** (114.8 g, 71%) as a pale yellow crystal. Mp. 102 - 104°C, ^{1}H-NMR ($CDCl_3$) 1.36 (s, 9H), 1.41 (s, 3H), 1.47 (s, 3H), 2.16 (s, 1H), 3.92 (dd, *J* = 5.8Hz, 8.4Hz, 1H), 4.03 (dd, J = 5.7Hz, 9.5Hz, 1H), 4.12 (dd, *J* = 5.5Hz, 9.5Hz, 1H), 4.19 (dd, *J* = 6.5Hz, 8.6Hz, 1H), 4.52 (m, 1H), 6.77 (s, 1H), 6.99 (m, 2H), 7.50 (m, 2H), 7.90 (m, 2H), 7.96 (m, 2H). ^{13}C-NMR ($CDCl_3$) 25.34, 26.79, 31.17, 35.06, 66.71, 68.90, 73.76, 92.17, 109.92, 114.50, 125.62, 126.92, 129.92, 132.75, 156.03, 162.04, 184.40, 185.61. MS: 410 (M^+), 335, 309, 277, 235, 203, 161, 101, 57. Anal. calcd. for $C_{25}H_{30}O_5$: C 73.15, H 7.37; found: C 73.18, H 7.36.

4-[(2,2-Dimethyl-1,3-dioxoran-4-yl)methoxy]-4'-methyldibenzoylmethane (**7b**): 4-Methylacetophenone **6b** (53.6 g, 0.4 mol) and **5** (112 g, 0.4 mol) were treated in a similar to the general procedure to give **7b** (66.4 g, 45%) as a pale yellow crystal. Mp. 88 - 90°C, ^{1}H-NMR ($CDCl_3$) 1.41 (s, 3H), 1.47(s, 3H), 2.42 (s, 3H), 3.92 (dd, *J* = 5.8Hz, 8.5Hz, 1H), (m, 2H), 4.02 (dd, *J* = 5.7Hz, 9.6Hz, 1H), 4.12 (dd, *J* = 5.5Hz, 9.6Hz, 1H), 4.18 (dd, *J* = 6.5HZ, 8.5Hz, 1H), 4.51 (m, 1H), 6.76 (s, 1H), 6.97 (m, 2H), 7.26 (m, 2H), 7.87 (m, 2H), 7.87 (m, 2H), 7.96 (m, 2H). ^{13}C-NMR ($CDCl_3$) 21.63, 25.35, 26.80, 66.72, 68.92, 73.87, 92.06, 109.93, 114.51, 127.09, 128.72, 129.22, 127.37, 129.44, 132.84, 142.98, 162.05, 184.53, 185.47. MS: 368 (M^+), 293, 267, 235, 161, 101, 57. Anal. calcd. for $C_{22}H_{24}O_5$: C 71.72, H 6.57; found: C 71.72, H 6.55.

4-(2,2-Dimethyl-1,3-dioxoran-4-yl)methoxy]-4'-methoxydibenzoylmethane (**7c**): 4-Methoxyaceto-phenone **6c** (60.0 g, 0.4 mol) and **5** (112 g, 0.4 mol) were treated in a similar to the general procedure to give **7c** (73.6 g, 48%) as a pale yellow crystal. Mp. 119 - 121°C, ^{1}H-NMR ($CDCl_3$) 1.41 (s, 3H), 1.47 (s, 3H), 3.88 (s, 3H), 3.92 (dd, *J* = 5.8Hz, 8.5Hz, 1H), 3.81 (m, 2H), 4.02 (dd, *J* = 5.7Hz, 9.5Hz, 1H), 4.12 (m, 1H), 4.19 (dd, *J* = 6.5Hz, 8.6Hz, 1H), 4.50 (m, 1H), 6.70 (s, 1H), 6.98 (m, 2H), 7.94 (m, 2H). ^{13}C-NMR ($CDCl_3$) 25.36, 26.81, 55.49, 66.73, 68.92, 73.88, 91.56, 109.94, 113.93, 113.97, 114.44, 114.50, 128.20, 128.66, 129.08, 129.12, 131.36, 161.94, 163.08, 184.42, 184.76. MS: 384 (M^+), 309, 270, 235, 177, 135, 101, 73, 43. Anal. calcd. for $C_{22}H_{24}O_6$: C 64.74, H 6.29; found: C 64.76, H 6.31.

4-[(2,2-Dimethyl-1,3-dioxoran-4-yl)methoxy]-4'-ethoxydibenzoylmethane (**7d**): 4-Ethoxyacetophenone **6d** (32.8 g, 0.2 mol) and **5** (56.0 g, 0.2 mol) were treated in similar manner to the general procedure to give **7d** (32.6 g, 41%) as a pale yellow crystal. Mp. 119 - 121°C, ^{1}H-NMR ($CDCl_3$) 1.39 (s, 3H), 1.45 (t, *J* = 6.9Hz, 3H), 1.41 (s, 3H), 1.47 (s, 3H), 3.92 (dd, *J* = 5.8Hz, 8.5Hz, 1H), 4.02 (dd, *J* = 5.8Hz, 9.6Hz, 1H), 4.12 (m, 3H), 4.18 (dd, *J* = 6.5Hz, 8.5Hz, 1H), 4.50 (m, 1H), 6.72 (s, 1H), 6.95 (m, 4H), 7.94 (m, 4H). ^{13}C-NMR ($CDCl_3$) 14.70, 25.36, 26.81, 63.76, 66.73, 68.92, 73.83, 91.52, 109.93, 114.11, 114.35, 114.42, 114.49, 127.97, 128.68, 129.07, 129.12, 131.35, 161.92, 162.52, 184.36, 184.82. MS: 398 (M^+), 265, 235, 191, 149, 101, 57. Anal. calcd. for $C_{23}H_{26}O_6$: C 69.33, H 6.58; found: C 69.34, H 6.60.

4-[(2,2-Dimethyl-1,3-dioxoran-4-yl)methoxy]-4'-(2-ethoxyethoxy)dibenzoylmethane (**7e**): Ethyl 4-

ethoxyethoxybenzoate (41.6 g, 0.2 mol) and **5** (56.0 g, 0.2 mol) were treated in similar to the general procedure to give **7e** (37.2 g, 42%) as a pale yellow crystal. Mp. 83 - 85°C , ^{1}H-NMR ($CDCl_3$) 1.25 (t, *J* = 7.0Hz, 3H), 1.41 (s, 3H), 1.47 (s, 3H), 3.61 (q, *J* = 7.0Hz, 2H), (m, 2H), 3.81 (m, 2H), 4.02 (dd, *J* = 5.7Hz, 9.5Hz, 1H), 4.12 (dd, *J* =5 .5Hz, 9.6Hz, 1H), 4.18 (m, 3H), 4.50 (m, 1H), 6.72 (s, 1H), 6.99 (m, 4H), 7.94 (m, 4H). ^{13}C-NMR ($CDCl_3$) 15.14, 25.33, 26.78, 66.69, 66.92, 67.67, 68.63, 68.73, 68.89, 73.85, 91.55, 109.90, 114.42, 114.47, 114.57, 128.24, 128.62, 129.05, 129.06, 131,26, 131.31, 161.92, 162.34, 184.42, 184.67. MS: 442 (M^+), 400, 367, 328, 235, 193, 159, 133. Anal. calcd. for $C_{25}H_{30}O7$: C 67.86, H 6.83; found: C 67.88, H 6.86.

General procedure of **1**

4-[(2,3-Dihydroxypropoxy)-4'-(1,1-Dimethyl-ethyl)dibenzoylmethane (**1a**): In a 3-L glass vessel, **7a** (100 g, 244 mmol), dioxane (800 mL), and a 1*N* HCl solution (200 mL) were added, and the reaction mixture was stirred at room temperature for 20 h. After the reaction mixture was neutralized by $NaHCO_3$, the solvent was removed under reduced pressure and the residue was extracted by EtOAc and washed with saturated NaCl solution, dried with $MgSO_4$. After the solvent was recovered under reduced pressure, the crude product was recrystallized from EtOH to give **1a** (80.0 g, 89%) as pale yellow crystals. Mp.124 - 126°C, ^{1}H-NMR ($CDCl_3$) 1.36 (s, 9H), 1.65 (brs, 1H), 2.10 (brs, 1H), 2.65 (brs, 1H), 3.79 (dd, *J* = 4.7Hz, 11.1Hz, 1H), 3.87 (m, 1H), 4.13 (m, 3H), 6.77 (s, 2H), 6.99 (d, *J* = .8Hz, 2H), 7.50 (d, *J* = 8.5Hz, 2H), 7.91 (d, *J* = 8.4Hz, 2H), 7.97 (d, *J* = 8.7Hz, 2H). ^{13}C-NMR ($CDCl_3$) 31.03, 31.13, 35.07, 63.49, 69.27, 70.25, 92.19, 114.49, 125.63, 125.73, 126.93, 128.92, 129.27, 132.71, 156.06, 161.89. MS: 370 (M^+), 295, 239, 195, 121, 94, 57. Anal. calcd. for $C_{22}H_{26}O_5$: C 71.33, H 7.07; found: C 71.34, H 7.08.

(2,3-Dihydroxypropoxy)-4'-methyldibenzoyl-methane (**1b**): **7b** (58.1 g, 157.9 mol) was treated in similar to the general procedure to give **1b** (47.6 g, 92%) as a pale yellow crystal. Mp. 135 - 137°C, ^{1}H-NMR (CD_3OD) 2.42 (s, 3H), 3.68 (m, 2H), 4.00 (m, 1H), 4.07 (dd, *J* = 6.0Hz, 9.8Hz 1H), 6.97 (m, 1H), 7.08 (m, 2H), 7.33 (m, 2H), 7.94 (m, 2H), 8.04 (m, 2H). ^{13}C-NMR (CD_3OD) 24.13, 66.59, 73.15, 74.19, 118.20, 132.95. MS: 328 (M^+), 294, 253, 240, 195, 161, 138. Anal. calcd. for $C_{19}H_{20}O_5$: C 69.50, H 6.14; found: C 69.52, H 6.15.

4-[(2,3-Dihydroxypropoxy)-4'-methoxydibenzoyl-methane (**1c**): **7c** (70.0 g, 182.4 mol) was treated in similar to the general procedure to give **1c** (56. 6 g, 90%) as a pale yellow crystal. Mp. 118 - 120°C, 1H-NMR [$(CD_3)_2SO$] 3.49 (m, 2H), 3.85 (m, 1H), 3.87 (s, 3H), 4.00 (dd, *J* = 6.2Hz, 10.1Hz, 1H), 4.13 (dd, *J* = 4.2Hz, 10.1Hz, 1H), 4.58 (m, 1H), 4.88 (d, *J* = 5.2Hz, 1H), 7.03 - 7.15 (m, 5H), 7.93 - 8.15 (m, 4H). ^{13}C-NMR [$(CD_3)_2SO$] 55.36, 62.50, 69.69, 69.74, 69.87, 91.36, 113.81, 113.95, 114.31, 114.46, 127.13, 129.19, 162.44, 162.83, 183.98. MS: 344 (M^+), 312, 270, 256, 210, 195, 166, 149, 135. Anal. calcd. for $C_{19}H_{20}O_6$: C 66.27, H 5.85; found: C 66.30, H 5.87.

4-(2,3-Dihydroxypropoxy)-4'-ethoxyldibenzoyl-methane (**1d**)**: 7d** (16.0g, 40.2 mol) was treated in similar to the general procedure to give **1d** (12.9g, 90%) as a pale yellow crystal. M.p. 134 - 136°C, ^{1}H-NMR (CD_3OD) 1.42 (t, *J* = 6.9Hz, 3H), 3.69 (m, 2H), 3.99 - 4.18 (m, 5H), 6.98 - 7.06 (m, 4H), 7.96 - 8.03 (m, 4H). ^{13}C-NMR (CD_3OD) 14.99, 64.03, 64.84, 70.56, 71.63, 115.48, 115.60, 130.28, 164.01, 164.11. MS: 358 (M^+), 284, 255, 195, 149, 121, 94, 45. Anal. calcd. for $C_{20}H_{22}O_6$: C 67.03, H 6.19; found: C 67.06, H 6.20.

4-[(2,3-Dihydroxypropoxy)-4'-(2-ethoxyethoxy)-dibenzoylmethane (**1e**): **7e** (30.0 g, 75.5 mol) was treated by similar manner as above to give **1e** (28.9 g, 93%) as a pale yellow crystal. Mp. 115 - 117°C, ^{1}H-NMR (CD_3OD) 1.22 (t, *J* = 7.0Hz, 3H), 1.65 (brs, 1H), 3.61 (q, *J* = 7.0Hz, 2H), 3.82 (m, 2H), 4.03 (m, 2H), 4.18 (m, 3H), 4.55 (s, 1H), 6.93 (s, 1H), 7.06 (m, 4H), 8.03 (m, 4H). ^{13}C-NMR (CD_3OD) 15.39, 64.03, 67.77, 68.81, 69.96, 70.57, 71.62, 92.37, 115.61, 129.38, 130.38, 163.93, 164.03 MS: 402 (M^+), 344, 255, 195, 163, 121. Anal. calcd. for $C_{22}H_{26}O_7$: C 65.66, H 6.51; found: C 65.67, H 6.53.

Another procedure of **7a**

(Oxoranylmethoxy)acetophenone (**9**): The mixture of 4-hydroxyacetophenone **8** (100 g, 0.735 mol), K_2CO_3 (53.5 g, 0.386 mol), epichlorohydrine 3 (136 g, 1.47 mol) and EtOH (500 mL) was stirred at 80°C for 2 h. After the EtOH was removed, toluene (500 mL) was added, then washed with water. The organic layer was concentrated and the residue was distilled to give **9** as a colorless oily product. (101 g, 72%) Bp. 157°C/0.9 Torr. ^{1}H-NMR ($CDCl_3$) 2.56 (s, 3H), 2.77 dd, *J* = 2.7Hz, 4.9Hz, 1H), 2.93 (dd, *J* = 4.7Hz, 5.6Hz, 1H), 3.37 (m, 1H), 4.00 (dd, *J* = 5.7Hz, 11.1Hz, 1H), 4.32 (dd, *J* = 2.9Hz, 11.0Hz, 1H), 6.95 (m, 2H), 7.94 (m, 2H). ^{13}C-NMR ($CDCl_3$) 26.32, 44.55, 49.88, 68.85, 114.25, 130.59, 130.63, 130.76, 130.90, 162.29, 196.74. MS: 192 (M^+), 177, 161, 147, 121, 93, 57. HRMS calcd. for $C_{11}H_{12}O_3$: 192.0786 ; found: 192.0788.

4-[(2,2-Dimetyl-1,3-dioxyran-4-yl)methoxy]aceto-phenone (**10**): In a 3-L glass vessel, **9** (101 g, 0.521 mol), acetone (900 mL) and a 3%H_2SO_4 aqueous solution (212 g) were added and the reaction mixture was stirred at 60°C for 4 hr. After the reaction mixture was neutralized by Na_2CO_3, it was washed

with a saturated NaCl aqueous solution. The organic layer was concentrated under reduced pressure, then toluene (500 mL) was added. The water was removed from the mixture. The residual salts were filtered and then acetone (1 L) and 98% H_2SO_4 (2 g) were added and stirred overnight at room temperature. After the reaction mixture was neutralized by Na_2CO_3 and concentrated at reduce pressure. Toluene (500 mL) was added to the residue and washed with water. The organic layer was concentrated under reduced pressure and isopropyl ether (300 mL) was added to afford **10** as a white crystalline solid (96 g, 73%). Mp.46 - 48°C, ^{1}H-NMR ($CDCl_3$) 1.41 (s, 3H), 1.47 (s, 3H), 2.55 (s, 3H), 3.91 (dd, *J* = 5.4Hz, 8.7Hz, 1H), 4.02 (dd, *J* = 5.3Hz, 9.6Hz), 4.11 (dd, J = 5.4Hz, 9.6Hz, 1H), 4.18(dd, *J* = 6.4Hz, 1H), 4.50 (d, *J* = 6.1Hz, 1H), 6.96 (m, 2H), 7.94 (m, 2H). ^{13}C-NMR ($CDCl_3$) 25.29, 26.31, 26.75, 66.64, 68.84, 73.80, 109.88, 114.21, 130.51, 130.54, 130.58, 130.70, 162.38, 196.64. MS: 250 (M^+), 235, 193, 175, 133, 101, 73, 43. HRMS calcd. for $C_{14}H_{18}O_4$: 250.1205 ; found: 250.1207.

4-[(2,2-Dimethyl-1,3-dioxyran-4-yl)methoxy]-4'-(1,1-Dimethylethyl)dibenzoylmethane (**7a**): In a 2-L glass vessel, $NaNH_2$ (7.8 g, 0.2 mol) and toluene (200 mL) were added. **10** (112 g, 0.4 mol) dissolved in toluene (200 mL) was dropwise added in the suspension for 30 min under N_2 gas. After stirring for 1 h, methyl 4-*t*-butylbenzoate **11** (19.2 g, 0.1mol) was added and stirred for 24 h. Toluene (200 mL) and dil. HCl (800 mL) were added to the reaction mixture, the organic layer was extracted, washed and the solvent was recovered under reduced pressure. The residue was recrystallized from EtOH to give **7a** (17.6 g, 43%)

IV. CONCLUSIONS

The authors have synthesized some novel dibenzoylmethane derivatives having a glyceryloxy group at the 4-position and it was found that they have excellent solubilities in oily and water-soluble bases and extremely useful as UV absorbers in the UV-A region that absorbs UV rays for cosmetics, etc.

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