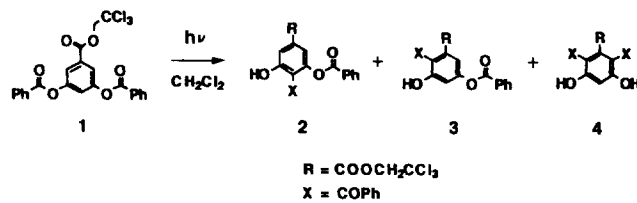


Photochemical Rearrangement of 2,2,2-Trichloroethyl 3,5-Bis(benzoyloxy) benzoate

Jeong-Mi Moon, Il Cheol Jeon*, and Sung Sik Kim*†

Department of Chemistry, Chonbuk National University,
Chonju 560-756, Korea

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Scheme 1.

A common photoprocess of aromatic compounds is lateral-nuclear rearrangement. One of the most extensively investigated reactions of this type is the photo-Fries rearrangement of O-aryl esters which, by a formal 1,3- or 1,5-acyl shift, produces a mixture of *ortho* and *para* acylphenols.¹⁻⁹ The photorearrangement can be made almost entirely *ortho* by cyclodextrin encapsulation.⁹ When phenyl carboxylate is irradiated in the cavity of cyclodextrin, it is possible to generate regio- or stereoselective products on the guest, in which the *para* isomer predominates.¹⁰ This rearrangement depends on the light absorption by the aryloxy moiety and occurs intramolecularly from the S_1 (π, π^*) state.²

We now report photochemical rearrangement of an aryl ester, 2,2,2-trichloroethyl 3,5-bis(benzoyloxy) benzoate (TBB) **1**, that is a precursor of dendritic macromolecules.^{11,12} TBB **1** has $\text{CO}_2\text{CH}_2\text{CCl}_3$ at *meta* position with respect to the two OCOPh groups. Thus, we expected that it would be possible to get *ortho* rearrangement product(s) exclusively by just irradiating **1** with UV light, without using any catalyst, because steric hindrance caused by the two substituents, $\text{CO}_2\text{CH}_2\text{CCl}_3$ group and the remaining OCOPh group inhibits formation of the *para* product. The ester **1** is actually too large to enter the cavity of cyclodextrin.

TBB **1** was synthesized from a reaction with benzoic acid and 2,2,2-trichloroethyl 3,5-dihydroxybenzoate in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) in dichloromethane.^{13,14} Irradiation of TBB **1** (100 mg, 0.20 mmol) in dichloromethane (200 mL) under N_2 with 300 nm UV light (band width at base line: 84 nm, Model RUL-3000 Å lamps in a Rayonet Photochemical Reactor, RPR-208) for 12 h afforded three kinds of photo-Fries rearrangement products, not only *ortho* rearrangement products, **2**¹⁵ and **3**,¹⁶ but also a double *ortho* rearrangement product **4**¹⁷ in 27%, 18%, and 10% yield, respectively. Analysis of the relative amounts of reaction mixture was carried out using HPLC (column: Sil-5B, Eluent: *n*-hexane/diethyl ether 1:1 (v/v), flow rate: 2 mL/min, detector: 280 nm UV). The crude products were isolated by flash chromatography (silica gel, 230-400 mesh) eluting with 19:1 *n*-hexane/ethyl acetate. The amount of ethyl acetate increased to 60% of the total eluents to give the products. About 30% of TBB **1** was recovered.

Photolysis of TBB **1** results in the formation of benzoyl radical and then the *ortho* rearrangement to give hydroxyaromatic ketone **2** as a major product. Another isomer **3** is also formed *via* *ortho* rearrangement of benzoyl radical. It was found that *para* rearrangement of benzoyl radical is not favorable, because of the steric hindrance, as mentioned

above. Double *ortho* rearrangement of two benzoyl radical leads to dihydroxyaromatic ketone **4**. ¹H NMR spectrum of **2** shows a broad singlet peak of hydroxyl group at 10.13 ppm in chloroform-*d*. ¹³C NMR spectrum (CDCl_3) of **2** was obtained, in which two carbon peaks (2 ArH's) of the central aromatic ring were observed at 117.26 and 115.28 ppm. Whereas, that of **3** shows two carbon peaks at 115.65 and 115.52 ppm. This implies that the electron densities of the two carbons of **3** are more close to each other than those of **2**. Mass spectra were also obtained to identify the three photoproducts. EI mass spectrum of **2** shows molecular ion peak at *m/e* 492. The peaks at *m/e* 77 and *m/e* 105 (100%) are quite diagnostic for benzoyl group (PhCO). A peak at *m/e* 345 (M-147) demonstrates that OCH_2CCl_3 group is remained in the structure. The ratio of relative abundance of the peaks at M, M+2, M+4 and M+6 is about 27:27:9:1, which accounts for the presence of three chlorine atoms in the photoproduct **2**. The same pattern was also observed in mass spectrum of **3**, in which a peak at *m/e* 105 was also the most prominent peak, *i.e.*, the base peak. However, in the case of **4**, the base peak was found at *m/e* 239, *i.e.*, M-253, resulting from elimination of PhCHO and OCH_2CCl_3 . The molecular ion peak of **4** was found at *m/e* 492. ¹H NMR spectrum (CDCl_3) of **4** shows doublet (4×PhH), doublet (2×PhH), doublet of doublet (4×PhH), and singlet peak (1×ArH) at 7.64, 7.47, 7.42, and 6.93 ppm, respectively, because of the symmetric structure of **4**. The photoproducts, **2**, **3**, and **4**, show the same fluorescence emission bands at 297, 308, and 322 nm in methanol at room temperature. The longest absorption maxima of **2**, **3**, and **4**, were found at 309, 309, and 316 nm in methanol, respectively. The difference ($\Delta\lambda_{\text{max}}=7$ nm) between the longest absorption maximum of **4** and those of **2** and **3** may be due to the additional benzoyl moiety of **4** which has two benzoyl groups as chromophores.

This photorearrangement provides a convenient route to the synthesis of various kinds of hydroxyaromatic ketones. Extension of the photochemical properties of aryl esters will be investigated.

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*† Author to whom correspondence should be addressed.

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14. UV absorption spectrum of **1** was not presented in ref. 13: UV (MeOH), λ_{max} 277, 235, 206 nm.
15. Spectral data of **2**: UV (MeOH), λ_{max} 309, 256, 240, 216, 212, 205, 201 nm; Fluorescence (MeOH), λ_{em} 322, 308, 297 nm (λ_{ex} 255 nm); IR (KBr), 3254 (br), 3064, 2959, 1735, 1630, 1567, 1447, 1370, 1250, 1208, 1068, 941, 899, 821, 763, 702 cm^{-1} ; 1H NMR ($CDCl_3$), δ 10.13 (bs, 1H, 1 x OH), 7.77 (s, 1H, 1 x ArH), 7.64-7.23 ppm (m, 11H, 10 x PhH and 1 x ArH), 5.00 ppm (s, 2H, CH_2CCl_3), ^{13}C NMR ($CDCl_3$), δ 163.18, 160.72, 150.07, 138.79, 133.76, 132.77, 129.75, 128.65, 128.30, 128.03, 117.26, 115.28, 94.55, 74.78 ppm; Mass (EI), m/e 492 (M), 345 (M-147), 105 (100%, PhCO), 77 (Ph).
16. Spectral data of **3**: UV (MeOH), λ_{max} 309, 254, 238, 213, 210, 209, 203 nm; Fluorescence (MeOH), λ_{em} 322, 308, 297 nm (λ_{ex} 255 nm); IR (KBr), 3254 (br), 3065, 2959, 1743, 1665, 1588, 1440, 1370, 1320, 1250, 1124, 1060, 927, 772, 709 cm^{-1} ; 1H NMR ($CDCl_3$), δ 9.50 (bs, 1H, 1 x OH), 8.22 (2 d's, 2H, 2 x ArH), 7.75-7.40 (m, 10H, 10 x PhH), 4.31 ppm (s, 2H, CH_2CCl_3); ^{13}C NMR ($CDCl_3$), 164.04, 159.92, 153.90, 138.76, 134.19, 133.84, 133.22, 130.36, 128.76, 128.68, 115.65, 115.52, 94.09, 74.54 ppm; Mass (EI), m/e 492 (M), 345 (M-147), 239 (M-PhCHO- OCH_2CCl_3), 105 (100%, PhCO), 77 (Ph).
17. Spectral data of **4**: UV (MeOH), λ_{max} 316, 266, 250, 219, 215, 203 nm; Fluorescence (MeOH), λ_{em} 322, 308, 297 nm (λ_{ex} 255 nm); IR (KBr), 3332 (br), 3064, 2924, 1743, 1616, 1447, 1377, 1264, 1215, 1131, 1025, 920, 860, 818, 770 cm^{-1} ; 1H NMR ($CDCl_3$), δ 10.62 (bs, 2H, 2 x OH), 7.64 (d, 4H, 4 x PhH), 7.47 (d, 2H, 2 x PhH), 7.42 (dd, 4H, 4 x PhH), 6.93 (s, 1H, ArH), 4.94 ppm (s, 2H, CH_2CCl_3); Mass (EI), m/e 492 (M), 239 (100%, M-PhCHO- OCH_2CCl_3), 105 (PhCO), 77 (Ph).

Preparation of Photosensitive Poly(urethane-imide)s Having Cyclobutane Rings and Their Properties

Kyu Ho Chae*, Jong Shin Park†, and Jin Soon Chung†

Department of Polymer Engineering,
Chonnam National University,
Kwangju 500-757, Korea

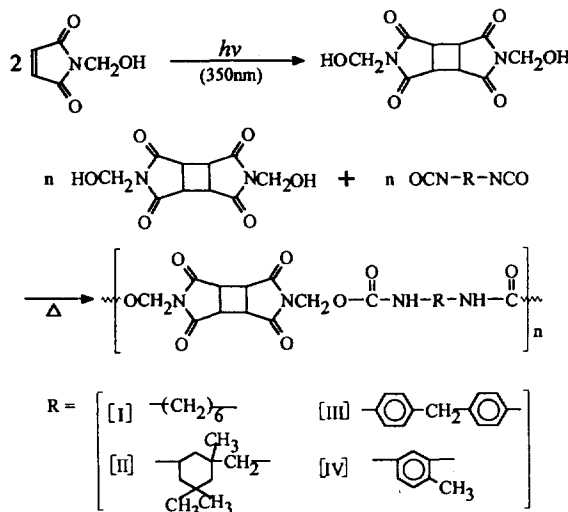
†Department of Chemistry, Chonnam National University,
Kwangju 500-757, Korea

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Polymer materials for electronic applications are required to have the properties of both easy processibility and thermal stability with low water absorption. Recently, the use of polyimides as polymer materials for electronic applications has become increasingly important because it simplifies the VLSI fabrication process.¹⁻³ Polyimides are well known not only for their chemical and thermal stabilities but also for their excellent electrical and mechanical properties. However, polyimides usually suffer from processing problems due to their insolubility and infusibility. In order to overcome these drawbacks, solvent soluble⁴ or modified polyimides⁵ have been developed.

In the previous studies at this laboratory we have reported the preparation and properties of photosensitive polyimides having cyclobutane ring structure.⁶ The present communication deals with the preparation method and properties of a modified photosensitive polyimide, poly(urethane-imide)s, having cyclobutane rings in the main chain.

The synthetic route of poly(urethane-imide)s (PUIs) having cyclobutane ring is shown in Scheme 1. The N-methylol maleimide cyclobutane dimer (MCD)⁷ was obtained by irradiation of N-methylol maleimide⁸ with 350 nm UV light in CH_2Cl_2 . PUI was prepared by reacting 1.27 g (5 mmol) of MCD with an equimolar amount of corresponding diisocyanate in 10 mL of N-methyl-2-pyrrolidone (NMP) at 60-110 °C for 2 hours. The polymer was purified after precipitation



Scheme 1.