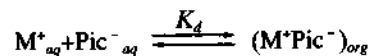
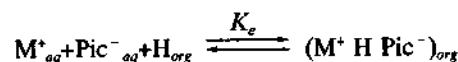
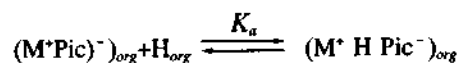


7. For a review see: Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178-184.
8. Yields were not optimized and all new hosts were fully characterized by ^1H NMR, ^{13}C NMR, IR and elemental analysis. Mp: **1a** 130-131 °C; **1b** 114-116 °C; **1c** 101-103 °C; **1d** 162-164 °C; **1e** 290-293 °C; **1f** 142-144 °C; **1g** 130-132 °C.
9. For reviews see: (a) Rebek, J., Jr. *Top. Curr. Chem.* **1988**, *149*, 189-210. (b) Rebek, J., Jr. *Chemtracts* **1989**, *2*, 337-352. (c) Rebek, J., Jr. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 245-255.
10. (a) For synthetic receptors for binding of alkali metal cations, see: (a) Jeong, K-S.; Pyun, S. Y. *Tetrahedron Lett.* **1994**, *35*, 7041-7044. (b) Jeong, K-S.; Cho, Y. L.; Pyun, S. Y. *Tetrahedron Lett.* **1995**, *36*, 2827-2830. (c) Commentary on 8b: Bolin, D. G.; Paquette, L. A. *Chemtracts* **1995**, *8*, 284-287.
11. The cation- π energy ($\Delta\Delta G$) has been calculated by assuming 1:1 complexes and employing the equations shown below.



Here, K_a (stability constant) = K_e (extraction constant) / K_d (distribution constant) and $\Delta\Delta G = \Delta G(\text{host } \mathbf{1e}) - \Delta G(\text{host } \mathbf{1a}) = -RT \ln\{K_a(\mathbf{1e})/K_a(\mathbf{1a})\}$. Since the distribution constant (K_d) must be identical under the same extraction conditions except the host (0.2 mM), $K_a(\mathbf{1e})/K_a(\mathbf{1a}) = K_e(\mathbf{1e})/K_e(\mathbf{1a})$ and thus $\Delta\Delta G = -RT \ln [K_e(\mathbf{1e})/K_e(\mathbf{1a})]$, where $K_e = [\text{M}^+ \cdot \text{H} \cdot \text{Pic}^-]_{\text{org}} / [\text{M}^+]_{\text{aq}} [\text{Pic}^-]_{\text{aq}} [\text{H}]_{\text{org}}$ at equilibrium. Therefore, the cation- π interaction in the host **1e** is -0.29 (Na⁺), -0.35 (K⁺), -0.28 (Rb⁺), and -0.24 kcal/mol (Cs⁺), respectively. The same treatments can be applied in the other hosts.

An Unusually Low Diastereoselectivity in the Photocyclization of *Ortho*-2,2,2-trifluoroethoxybenzophenone

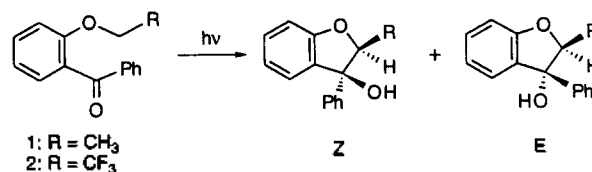
Tae Young Kim and Bong Ser Park*

Department of Chemistry, Dongguk University, Seoul 100-715, Korea

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The Yang reaction,¹ which produces cyclic alcohols via intramolecular hydrogen abstraction by excited ketones, has received a lot of attentions in both synthetic² and mechanistic³ aspects. Since it can give diastereomeric mixtures of the cyclic alcohols, many recent studies on the reaction have been oriented toward understanding the factors controlling diastereoselectivities in the photocyclization of various ketones.⁴ Recently Wagner has studied several ketones to give 1,5-biradical intermediates which then couple to form cyclic alkanols in varied diastereomeric ratios.⁵ The results have been analyzed in terms of conformational preferences that pre-exist in the biradicals and entropic factors related to intersystem crossing during the product formation. One system that they have looked at is *o*-alkoxybenzophenone, among which *o*-ethoxybenzophenone, **1**, gives diastereomeric dihydrobenzofuranols in an 11:1 *Z/E* ratio in benzene. In our lab, we have recently investigated the photoreactivity of *o*-2,2,2-trifluoroethoxybenzophenone, **2**, which is structurally related to **1**, and found a strikingly different ratio in the diastereomeric dihydrobenzofuranols. The result is described below (Scheme 1).

The starting ketone was prepared by stirring *o*-hydroxybenzophenone (1 eq.) and potassium carbonate (1.5 eq.) with excess amounts of 2,2,2-trifluoroethyl iodide (3 eq.) in DMF at 40 °C. After purification by column chromatography over silica gel using hexane and ethyl acetate



Scheme 1.

(10 to 1) as eluents, an oily product was obtained in 65% yield.⁷ The ketone was dissolved into 0.5 ml of benzene- d_6 and transferred to an NMR tube (0.2 M). After degassing by bubbling argon through for 10 minutes, the sample was subjected to photolysis using a Hanovia 450 W medium pressure mercury lamp with a Pyrex filter. After 50 minute irradiation, the reaction was completed and the formation of two isomeric products was apparent from its ^1H NMR spectrum (Figure 1).

Each product was confirmed by the usual spectroscopic methods and by comparing it with that of photoproduct from **1**.⁸ Assignment of stereochemistry of each isomer was made on the basis of the same criteria used for photoproducts from **1**, in which the chemical shifts of groups cis to a phenyl were more upfield than the one trans to it.

The ratio of *Z*- to *E*-2-trifluoromethyl-3-phenyldihydrobenzofuran-3-ol turned out to be 2 to 1 (by NMR in-

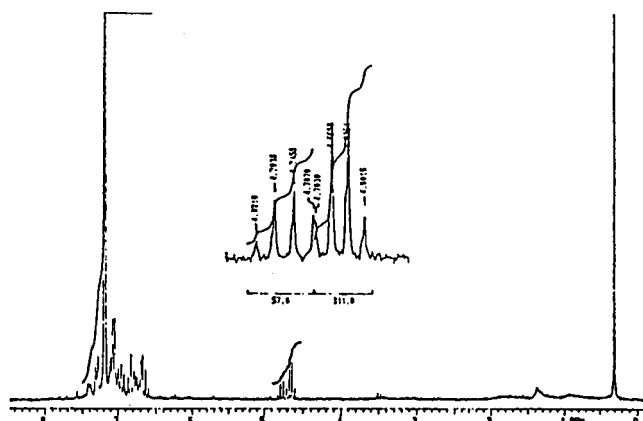
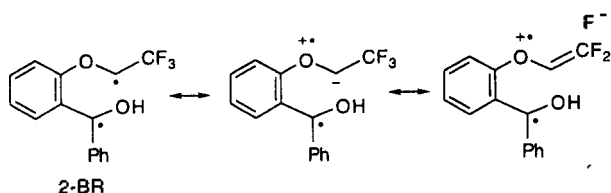


Figure 1.



Scheme 2.

tegration) when **2** was photolyzed in benzene. The ratio is remarkably different from that of photoproducts of **1**, which is 11 to 1 in benzene. It is hard to believe that a methyl and a trifluoromethyl show such a big difference in terms of nonbonded interaction. Besides, there is no precedent in the literature that a trifluoromethyl causes a significant change in intersystem crossing mechanism such as a spin orbit coupling. We believe some other factors are responsible for such a big difference in diastereoselectivities of **1** and **2**.

Wagner has reported some years ago that in the photochemistry of α -fluorovalerophenone and α,α -difluorovalerophenone the α -fluorines greatly influence the efficiency of the Yang cyclization.⁹ The author explained that the enhancement of cyclization over elimination was caused by preventing a preferred conformation for the elimination due to fluorine hyperconjugation. The effect of α -fluorines on product diastereoselectivity was not discussed in their studies.

As mentioned previously, **2** photocyclizes via an 1,5-biradical intermediate, **2-BR**. A radical site of **2-BR** has both alkoxy- and trifluoromethyl substituent, which can be considered as a push-pull type. Thus, this biradical may have extra stabilization which is better known as a captodative effect¹⁰ (Scheme 2).

It seems that the extra stabilization increases the lifetime of **2-BR** enough to change the stereochemical integrity of the cyclization and causes much lower *Z/E* ratio of the in-

danol products than that of **1**. The biradical would therefore have enough time to give the photoproducts more or less towards thermally equilibrated ratios. We are currently investigating the photochemical cyclization of several analogues of **2** to obtain further insights of this reaction mechanism.

In summary, the Yang reaction of **2** shows a remarkably different diastereoselectivity from that of **1**. The result has been explained by an unique manifestation of captodative effect of the biradical intermediate.

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7. Spectroscopic data of **2**; ¹H NMR (200 MHz, CDCl₃) δ 7.80 (2H, d, *J*=7.2 Hz), 7.39-7.61 (5H, m), 7.19 (1H, t, *J*=7.3 Hz), 6.99 (1H, d, *J*=7.3 Hz), 4.27 (2H, q, *J*=7.0 Hz), ¹³C NMR (56 MHz, CDCl₃) δ 196.0, 155.9, 138.1, 133.5, 132.5, 130.6, 130.3, 128.8, 123.5 (q, *J*=324.0 Hz), 123.3, 114.3, 67.2 (q, *J*=40.0 Hz). IR (CCl₄) 1670 (C=O) cm⁻¹. EI Mass 77, 105, 197, 280 (M⁺).
8. *Z*-2-trifluoromethyl-3-phenyldihydrobenzofuran-3-ol: ¹H NMR (200 MHz, C₆D₆) δ 7.29 (2H, d, *J*=7.2 Hz), 7.20-6.61 (7H, m), 4.65 (1H, q, *J*=6.7 Hz), *E*-2-trifluoromethyl-3-phenyldihydrobenzofuran-3-ol: ¹H NMR (200 MHz, C₆D₆) δ 7.39 (2H, d, *J*=7.2 Hz), 7.16-6.65 (7H, m), 4.65 (1H, q, *J*=7.5 Hz). For comparison, the spectroscopic data of photoproducts from **1** can be found in ref. 6.
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