

showed 60-67% yield at 0 °C and 48-53% yield at room temperature. Cinnamic acid, an α,β -unsaturated aromatic carboxylic acid, was converted into the corresponding unsaturated aldehyde in a 48% yield at 0 °C and a 40% yield at room temperature.

It was interesting that the reduction rates of aromatic carboxylic acids were somewhat faster than those of aliphatic acids. These phenomena were sometimes found in the systematic studies for the reduction of representative organic compounds with metal(lithium, sodium and potassium) gallium hydride,⁹ but the reason is unclear so far. In general, the yields for all reductions of carboxylic acids to aldehydes by lithium gallium hydride were better at 0 °C than at room temperature.

Lithium gallium hydride was prepared by the known method.¹⁰ And the following procedure for the reduction of benzoic acid was representative. An oven-dried, 50-mL flask, equipped with a side arm fitted rubber stopple, magnetic stirring bar and a reflux condenser connected to a mercury bubbler, was flushed with nitrogen and charged with 0.1253 g (1 mmol) of benzoic acid and 7 mL of diethyl ether. The flask was immersed into the ice water bath and a precooled solution of lithium gallium hydride (1.89 mL, 0.27 M, 0.5 mmol) in diethyl ether was added slowly with vigorous stirring. After 6 h, the reaction mixture was hydrolyzed with 10 mL of 2 N sulfuric acid and the suitable internal standard was added. The aqueous layer was saturated with sodium chloride and organic layer was subjected to GLC analysis on a Chromosorb-WHP, 10% Carbowax 20 M, 2 m, 1/8 inch column, indicating benzaldehyde in 67% yield.

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Photochemistry of α -(*o*-Tolyl)acetophenone Derivatives: Conformational Effects on the Photochemical Processes

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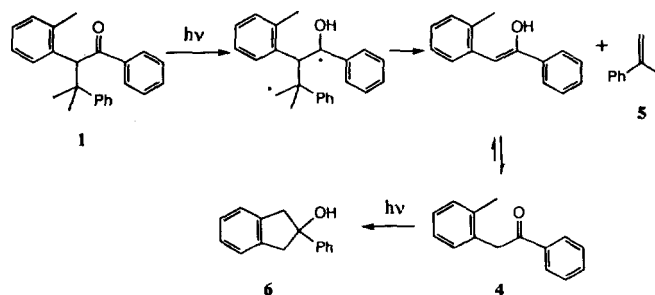
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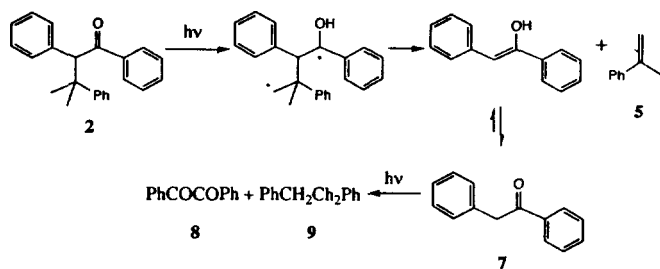
The correlation between structure and reactivity has been major interests for many years in studies of photochemical reaction.¹ For the photochemical reactions having several possible decay pathways, the product distribution of the reaction depends upon each decay rate for the excited state and barrier for conformational changes. When the molecule has high barrier for the conformational change, the reaction occurs mainly in the highly populated conformer in the ground states, assuming that it is the reactive one. Here we wish to report another example of so called "ground state control"² of photoreactivity.

Three α -arylacetophenone derivatives studied were synthesized³ and were irradiated by Pyrex filtered UV irradiation using Hanovia 450 W medium pressure mercury lamp. Prior to large scale reaction, the photoreaction was followed by NMR in benzene-*d*₆ and in methanol-*d*₄ solution. Structural assignments of photoproducts were made by comparing their spectroscopic data with those of authentic samples.⁴

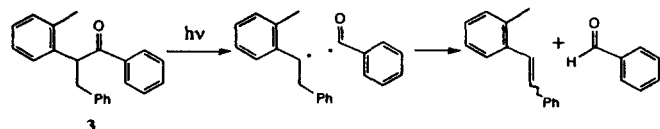
Scheme 1 summarizes the result of photolysis of compound 1 in benzene. When the irradiation was stopped before completion, initial growth of products 4 and 5 was noticeable. Further irradiation resulted in the formation of the secondary photoproduct (compound 6). There was no evidence of either Norrish type I α -cleavage or δ -hydrogen atom abstraction from benzylic position of α -tolyl group.



Scheme 1.



Scheme 2.



Scheme 3.

In methanol, the result was same as in benzene, which gave products 4 and 5 initially, followed by the formation of product 6 on prolonged irradiation. The quantum efficiency of the reaction was better in methanol than in benzene, which was consistent with the result of valerophenone.⁵

Compound 2 showed similar photochemical behavior as compound 1, except that the secondary photoreaction was different. Products 5 and 7 stayed for quite some time as major photoproducts. Prolonged irradiation caused slow formation of α -cleavage products 8 and 9. Scheme 2 shows the photobehavior of compound 2.

Irradiation of compound 3 resulted in the formation of Norrish type I reaction products (Scheme 3). There was no sign of δ -hydrogen atom abstraction from benzylic position of α -tolyl group.

Wagner has shown several ring substituted α -(*o*-tolyl)acetophenones undergo photocyclization to give 2-indanol derivatives in high quantum efficiency in solution and in high chemical yield in solids.⁶ The mechanism for this reaction involves triplet state δ -hydrogen abstraction that generates 1,5-biradical.

On the other hand, putting additional substituent on the α carbons of the acetophenone provided dramatic changes in the photoreactivity of the ketones.⁷ The major photoreaction was α -cleavage. This interesting phenomenon was soon rationalized based on the result from X-ray structure, NMR analysis as well as MMX calculation. For α -(*o*-tolyl)acetophenone, the most stable conformation has α aryl group eclipsing with C=O group, which is very close to "reactive" geometry. For the substituted ones, however, an additional α -substituent makes the tolyl group twist away from the carbonyl. The eclipsed geometries become too high in energy to be populated within the short triplet lifetimes and reaction has to occur from the highly twisted geometry. In this unfavored geometry for hydrogen abstraction, the reaction rate decreases and other reactions such as α -cleavage, start to compete.

Compounds 1, 2 and 3 share a common structural feature, which contain a sterically demanding group at α position of α -arylacetophenones. In addition, compounds 1 and 2 have γ -hydrogens, which can give type II reactivities. These compounds have, therefore, three possible reaction pathways; α -cleavage, H-abstraction from γ position and H-abstraction

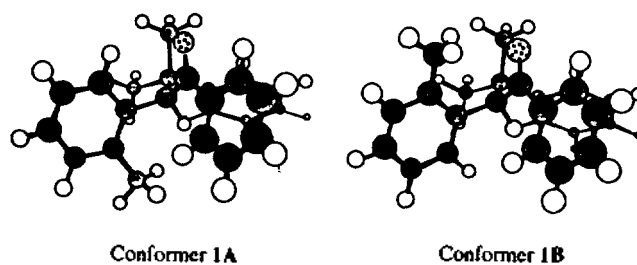


Figure 1.

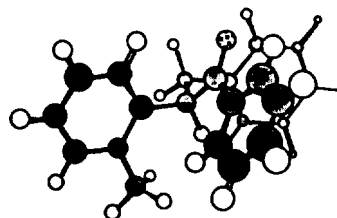


Figure 2.

from δ position. As shown above, compounds 1 and 2 undergo primarily type II H-abstraction without α cleavage. The rate constant of α cleavage for α substituted α -arylacetophenones are known to be about 10^7 sec^{-1} .⁸ This means that the rate constant of the observed hydrogen abstraction reaction of compounds 1 and 2 must be at least 10^8 sec^{-1} . The lack of hydrogen abstraction from benzylic position of *o*-tolyl group can be explained by the conformational preference of these molecules, *vide infra*.

We have performed the energy minimization of compound 1 using MM2 calculation. After minimization, we have obtained two minimum energy geometries shown in Figure 1. Conformer 1B has both γ and δ hydrogens within reacting distance from carbonyl oxygen, whereas conformer 1A has δ hydrogens far away from the reaction center. Energy difference between two conformers was calculated to be over 2 kcal/mol. The conformer 1B becomes relatively high in energy to be populated within the short triplet lifetimes and reaction has to occur from the conformer 1A. Even though absolute energy does not mean much in molecular mechanics calculation, the relative energy has been widely used to explain the experimental observations.⁹

The result of photolysis of compound 3 verifies that Norrish type I cleavage does occur for this type of molecule. Once again, hydrogen abstraction from benzylic position of *o*-tolyl group does not occur, which can be explained similarly to compound 1. Energy minimized structure of compound 3 is shown in Figure 2. The inert photoreactivity of the compound 3 in solid state can also be explained by the calculated geometry. In this geometry, the benzylic hydrogens are too far away from the carbonyl oxygen and the hydrogen abstraction cannot occur without extensive conformational change. Presumably, α cleavage products are not formed in solid state photolysis due to cage effect. Even if α cleavage does occur, the radicals recouple to give the starting material in the restricted media.

In summary, three α -arylacetophenone derivatives studied showed selective photoreactivities. The selectivity was explained in terms of conformational preference of the molecules

in the ground state. For better understanding of this selectivity, kinetic studies on these molecules are currently in progress.

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3. These compounds were synthesized by standard procedures; Compounds **1** and **2** were prepared by the condensation of acetone with the corresponding arylacetonitriles, and consecutive 1,4- and 1,2- addition of phenyl Grignard reagents, followed by hydrolysis. Overall isolated yields were 12 and 18%, respectively. Compound **3** was prepared by α -benzylation of *o*-tolylacetonitrile and 1,2- addition of phenyl Grignard reagent, followed by hydrolysis. Overall yield was 42%. Spectroscopic data of compound **1**; ^1H NMR (200 MHz, CDCl_3) δ 7.67 (2H, d), 7.1-7.5 (12H, m), 5.18 (1H, s), 2.09 (3H, s), 1.70 (3H, s), 1.50 (3H, s), IR (CCl_4), 1694 (C=O) cm^{-1} , Mass 77, 91, 105, 119, 210. Molecular ion peak was not detected. Spectroscopic data of compound **2**; ^1H NMR (200 MHz, CDCl_3) δ 7.72 (2H, d), 7.1-7.45 (13H, m), 5.00 (1H, s), 1.60 (3H, s), 1.43 (3H, s), IR (CCl_4), 1692 (C=O) cm^{-1} , Mass 77, 91, 105, 119, 196. Molecular ion peak was not detected. Spectroscopic data of compound **3**; ^1H NMR (200 MHz, CDCl_3) δ 7.77 (2H, d), 7.05-7.47 (12H, m), 4.93 (1H, dd, $J=6.5, 7.6$ Hz), 3.55 (1H, dd, $J=7.6, 13.6$ Hz), 2.95 (1H, dd, $J=6.5, 13.6$ Hz), 2.25 (3H, s), IR (CCl_4), 1688 (C=O) cm^{-1} , Mass 77, 91, 105, 195, 300 (M^+).
4. ^1H NMR spectra of authentic samples were obtained separately and were compared with those of photoproducts. These were also same as the published data. Ref. 6 and Pouchert, C. J.; Behnke, J. In *The Aldrich Library of ^{13}C and ^1H FT NMR Spectra*; Aldrich chemical Co. Inc.; Inc.; U.S.A.: 1993, Chemical yields of **5** and **6** in the photolysis of compound **1** were 40 and 45%, respectively. Chemical yields of **5**, **8** and **9** in the photolysis of compound **2** were 30, 10 and 12%, respectively.
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Radical Mediated Alkylations of Vinyl Epoxides

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The reaction of vinyl epoxides with various organometallic reagents such as organolithium,¹ organocopper,² and organopalladium reagents^{3,4} is very useful in organic synthesis. However, radical reactions of vinyl epoxides have received little attention.⁴ Recently, we have studied the radical reactions of vinyl epoxides utilizing 1,5-Bu₃Sn group or 1,5-hydrogen atom transfer.⁵

Concerning radical mediated alkylations of vinyl epoxides, it was reported that a cycloalkyl radical had attacked a vinyl epoxide to yield the allylic alcohol in only 13% yield.^{4a} The similar alkylation was also achieved with trialkylborane in the presence of oxygen.⁶ However, the yield was relatively low and the generality of the reaction was not demonstrated. Recently, radical alkylation of vinyl epoxides was successfully carried out with stable carbon-centered radicals using amineborane complex.⁷

In connection with our interest in radical reactions of vinyl epoxides,^{5,8} we studied the possibility of intermolecular radical alkylations of vinyl epoxides with alkyl radicals. However, initial results were discouraging. When the radical reactions of vinyl epoxides were carried out with alkyl iodides and Bu₃SnH/AIBN under highly diluted conditions using a syringe pump technique, alkyl radicals reacted with Bu₃SnH before attacking vinyl epoxides, yielding the direct reduction products along with the starting vinyl epoxides. Therefore, a clean generation of tributyltin radical in the absence of any efficient radical scavengers like Bu₃SnH was required. A recent report on selective homolytic cleavage of bis-tributyltin using a photosensitizer such as acetone or *p*-methoxyacetophenone under mild irradiation⁹ was suited for our purpose. Intermolecular radical alkylations involving the addition of alkyl radicals to the double bonds have been successfully performed using this procedure.¹⁰

When the radical reaction of acyclic vinyl epoxide **1** was carried out with ethyl iodide in benzene using bis-tributyltin/acetone/2-propanol system under irradiation (300 nm), **3b** was isolated in only 28% yield. The low yield with **1** may result from facile 1,5-hydrogen transfer in **2a** from carbon to oxygen as shown in Scheme 1. The resulting allylic radical **3a** would be reluctant to abstract hydrogen atom from 2-propanol due to its low reactivity. Much better results were obtained with endo vinyl epoxide **4**. When the radical reaction of **4** was carried out with ethyl iodide under the same conditions, the alkylated product **5a** was obtained in 63% yield along with **5b** (4%) and **5c** (9%) as side products. We envisioned that **5b** might be formed by ejection of hydrogen atom from an intermediate alkoxy radical and **5c** might result from attack of tributyltin radical to **4**, although an exact mechanism awaits further studies. As shown in Table 1, several alkyl iodides were employed and similar results were