Communications to the Editor

Bull. Korean Chem. Soc. **1995**, Vol. 16, No. 6   469

hydration shell increasing the dimer/monomer ratio to 4.8, as shown in Figure 2-(b). The decreased band area of monomeric forms is nearly the same as the half of the increased one of dimer. This result indicates that the PAS method can be applied to the quantitative investigation of the monomer-dimer equilibrium within zeolite.

The PA spectrum shown in Figure 2-(c) was obtained in N_2 atmosphere after partially dehydration in vacuum oven of 10^{-3} mmHg at 50 ℃ for 6 hours. The enhanced MBH^{2+} band could be attributed to the protons generated by the dissociation of water molecules resulted from the dehydration of CsY. The slightly increased monomer and the decreased dimer band (dimer/monomer=2.2) confirm the unique role of water having the high dielectric constant on dimerization of dye.[2,9] Most of the dissociated dimers were converted to the protonated monomer form as shown in the deconvolution bands (figure 2-(c)).

Figure 2-(d) illustrates the reversible dimerization of monomeric forms resulted from rehydration process. During the saturation of methanol less polar than water within the dehydrated sample (Figure 2-(e)), however, the dimerization did not proceed and the dimer band blue-shifted.

We obtained the following conclusions from the above results. (a) The dehydration process within CsY zeolite leads to the water dissociation. (b) While the shielding proton in hydrated sample could not contribute to the protonation of MB^+, the unshielded one in dehydrated sample reacted easily with MB^+ to form the MBH^{2+}. (c) The dimerization and protonation of methylene blue within CsY zeolite are reversibly proceeded by the hydration-dehydration.

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Facile Reduction of Carboxylic Acids to Aldehydes by Lithium Gallium Hydride

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A number of methods for the direct transformation of carboxylic acids into aldehydes by using lithium in methylamine,[1] diisobutylaluminum hydride,[2] thexylborane,[3] thexylhaloborane,[4] bis(4-methylpiperazinyl)aluminum hydride,[5] the Grignard reagent catalyzed by dichloro-bis(n-cyclopenta-dienyl)titanium or N,N-dimethylchloromethyleniminium chloride,[6] and lithium tri-*tert*-butoxyaluminum hydride,[7] and 9-borabicyclo[3.3.1]nonane(9-BBN) species[8] have been reported.

In the course of exploring the reducing properties of lithium gallium hydride, we observed that benzoic and caproic acids consumed one hydride rapidly for reduction, but the further reduction proceeded very slowly. These results suggested the possibility of aldehyde synthesis from carboxylic acid using this reagent.

The reduction of carboxylic acids were carried out by the addition of 0.5 equiv lithium gallium hydride in diethyl ether at 0 ℃ and room temperature. As shown in Table 1, aliphatic acids, such as acetic, hexanoic, and cyclohexanecarboxylic acids provided the corresponding alcohol in 73-75% yield at 0 ℃ and 62-68% yield at room temperature. An α,β-unsaturated aliphatic acid, crotonic acid was converted into the corresponding unsaturated aldehyde in a 70% yield at 0 ℃ and a 65% yield at room temperature. However, acrylic acid was converted into the corresponding unsaturated aldehyde in a 50% yield at 0 ℃ and a 48% yield at room temperature. The low yield of acrylic acid comparing with other carboxylic acids was presumably due to the attack of hydride on the double bond of the compound. Aromatic carboxylic acids, such as benzoic, 2-methylbenzoic and α-naphthoic acids,

Table 1. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids with LiGaH₄ in Diethyl Ether[a]

Acid	Time (h)	Yield of Aldehyde[b] (%) 0 ℃	Room Temperature
hexanoic	12	73	68
cyclohexanecarboxylic	12	73	65
crotonic	12	70	65
acetic	12	75[c]	62[c]
acrylic	12	50	48
benzoic	6	67	53
2-methylbenzoic	6	65	52
cinnamic	6	48	40
α-naphtoic	6	60	48

[a] Reacted with 2 equiv reagent in hydride for carboxylic acid. [b] Yields were estimated by GLC. [c] Yields were estimated by 2,4-dinitrophenylhydrazine.

showed 60-67% yield at 0 ℃ 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 ℃ 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 ℃ 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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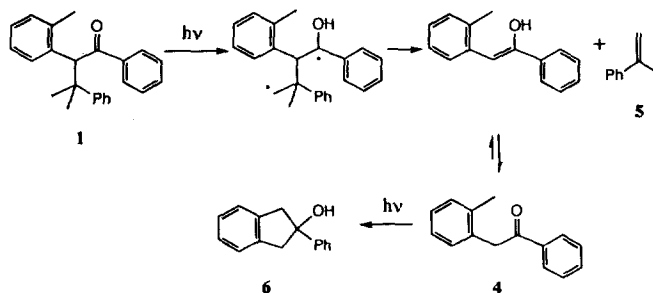*Department of Chemistry, Dongguk University, Seoul 100-715, Korea*
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The correlation between structure and reactivity has been major interests for many years in studies of photochemical reaction.[1] For the photochemical reactions having several possible 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 synthesized[3] 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-cleavge or δ-hydrogen atom abstraction from benzylic position of α-tolyl group.

Scheme 1.