# Notes

## Photochemistry of 5- *(o-* Tolyl)-5-cyano-4,4-dimethyl-2-pentanone

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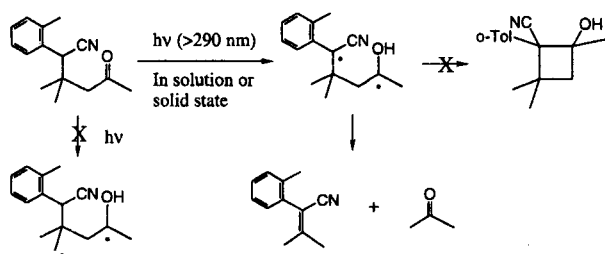[†]*Department of Chemistry Education, Seoul National University, Seoul 151-742, Korea*
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Photoinduced hydrogen abstraction reaction, which is better known as the Norrish type II reaction, has been a highlight in the development of a general picture of how photochemical reactions occur.[1] The rate constant for internal hydrogen abstraction depends on electronic configuration, on C-H bond strength or inductive substituent effects, and on confirmational factors. These factors will determine the observed product ratios of photoreactions where more than one product are possible.

When a molecule has confirmational preference in the ground state, reaction proceeds mainly in the geometry to induce selectivity. An extreme would be photoreactivity in solid state, where molecular motions are minimized. Thus, the photoreactivities in solid state, especially where the selective transformation occurs among several competitive pathways, have made it possible to predict the most stable geometry of the given molecules.[2] Here we wish to report another example of photoreactions which are dictated by conformational preference; a photoreactivity of 5-(o-tolyl)-5-cyano-4,4-dimethyl-2-pentanone (OTCMP) in solution and solid state.

OTCMP has been synthesized and irradiated as described in the experimental section. The results of photolysis of OTCMP are summarized in Scheme 1. In solution, 2- *(o-*tolyl)-3-methyl-2-butenenitrile and acetone were observed with a ratio of 1 to 1 as photoproducts *via* intramolecular hydrogen abstraction followed by elimination. The abstraction reaction occurred only at a carbon containing tolyl and cyano group. Among two possible routes from the 1,4-biradical intermediate, Norrish type II elimination reaction was predominant. No cyclization products were detected. The chemical yield of product formation in this reaction was almost quantitative. From parallel irradiation of OTCMP and valerophenone, the quantum yield was estimated to be 0.2 in benzene.

The reaction also preceded in solid state. The efficiency of the reaction was low as expected. At prolonged irradiation, the solid became liquid presumably due to formation of acetone as reaction proceeded.

The rate constant for internal hydrogen abstraction depends on electronic configuration, on C-H bond strength or inductive substituent effects, and on conformational factors.[1] It is well known that the electronic configuration of an n, $\pi^*$ state allows hydrogen abstraction processes of low activation energy to take place. In aliphatic ketones such as OTCMP, n, $\pi^*$ state singlets interact with C-H bonds as rapidly as do triplets because the intersystem crossing is so slow ($k_{ISC}$=1-5 x $10^8$ sec$^{-1}$, that intramolecular hydrogen abstraction reactions can compete with. (See below for the typical rate constants) Aryl ketones generally undergo intersystem crossing so rapidly that most of their photoreactions are triplet-derived.

Inasmuch as n, $\pi^*$ excitation of a carbonyl involves some loss of electron density from the oxygen n orbital, n, $\pi^*$ triplets respond to the inductive effects of substituents near the C-H bond being attacked. Substituent effects on hydrogen abstraction reaction have been studied and rate constants for $\gamma$-hydrogen abstraction of various ketones have been collected.

OTCMP has two different types of $\gamma$ hydrogens; One is just a methyl C-H and the other is a tertiary C-H containing a phenyl and a cyano group. Typical rate constants for $\gamma$-hydrogen abstraction by n, $\pi^*$ triplets of acyclic ketones are 1 x $10^7$, 1 x $10^8$ and 5 x $10^8$ sec$^{-1}$ for primary, secondary and tertiary C-H bonds, respectively.[3] A phenyl group activates the process by 40 times and a cyano group deactivates it by a half.[4] Taking all of these factors into consideration, the tertiary C-H containing a phenyl and a cyano group would be more activated than the primary C-H by three orders of magnitude. Even if we consider a statistical factor, which is six to one ratio of hydrogens, the difference remains still in two orders of magnitude. This may be why the reaction occurs predominantly in the tertiary C-H containing a phenyl and a cyano group.

The regioselectivity can also be explained by the entropy effect, which can be viewd as the probability that a molecule will attain the correct geometry for reaction. Intramolecular bifunctional interactions are subjected to some conformational limitations. The interacting groups must be able to rotate within a minimal distance of each other for proper orbital overlap and reaction.

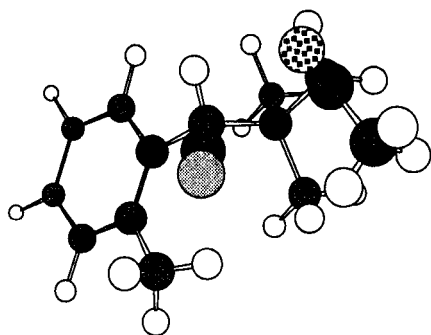Recently, Wagner has addressed the question of how



**Scheme 1.**

440 *Bull. Korean Chem. Soc.* **1997,** Vol. 18, No. 4

*Notes*



**Figure 1.**

rates of conformational change affect the course of photochemical reactions There are several possible routes that are derived from competition between confirmational change and excited state reaction. In most flexible acyclic systems, conformational equilibrium is established before reaction. Thus, the reaction rate is dependent upon how much the reactive conformers are populated in excited state. In order to test this idea, we performed a simple molecular mechanics calculation on OTCMP using MM$^+$ of HyperChem.[6]

The energy minimized structure of OTCMP shown in Figure 1 indicates that the hydrogen at the tertiary carbon is 2. 93 Å away from the carbonyl oxygen and hydrogens at the primary carbon are beyond reacting distance. Scheffer has suggested several important structural parameters for intramolecular hydrogen abstraction reactions of ketones.[7] Among these parameters, the most important one appears to be d, the distance between O and H. The theoretically 'ideal' d value is known to be <2.7 Å by Scheffer, but there have been several experimental observations that suggest the 'actual' d value to be <3.1 Å.[8] This general consideration is consistent with our observation on the solid state reactivity of OTCMP which gives selective hydrogen abstraction.

In Summary, OTCMP has been irradiated in both solution and solid state to result in a regioselective hydrogen abstraction reaction from a tertiary C-H containing a phenyl and a cyano group. Even though our results can be explained by C-H bond strength or inductive substituent effects, the energy minimized structure of OTCMP suggests that ground state confirmational preferences are dictating the observed reactivity at least in solid state where molecular motions are rather restricted. Further insights along this line are being made currently in our lab with other model compounds.

## Experimental

**General Procedure.** All $^1$H and $^{13}$C NMR spectra were obtained using a Varian Gemini-200 spectrometer in CDCl$_3$. All the IR spectra were recorded using solution in CCl$_4$ on a Bomem MB 100 spectrometer. Mass spectra were recorded on a Varian VG Trio 2000. The compound was irradiated by Pyrex filtered near 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. NMR tube scale irradiation was done as follows; An NMR tube containing sample solution (0.01-0.02 M in 0.75 mL of deu-

terated solvents) was degassed by bubbling argon through for 10 minutes. The NMR tube was attached to an immersion well by wire and was irradiated. Preparative scale irradiation was as follows; A large test tube containing sample solution (0.01-0.02 M in 70-100 mL) was fitted with a 24/40 rubber septum and the sample was degassed by bubbling argon through for 10 min. or throughout the irradiation. The test tube was attached to an immersion well by wire and was irradiated. Irradiation in solid state was performed by packing the sample into a melting point capillary tube and by attaching it to an immersion well. The irradiated capillary tube containing a sample was broken into pieces and it was extracted with a deuterated solvent. Structural assignments were made either by comparing with authentic samples or by their spectroscopic data.

**5-( *o*- tolyl)-5-cyano-4,4-dimethyl-2-pentanone (OTCMP).** The compound was prepared by stirring the mixture containing *o*- tolylacetonitrile, KF adsorbed onto alumina and excess acetone in DMF at 50 °C for 2 days. After purification by column chromatography using hexane and ethyl acetate (4 to 1) as eluents, OTCMP was obtained as white powder. mp 104.5 -105.5 °C, $^1$H NMR (CDCl$_3$) δ 7.42-7.20 (4H, m), 4.81 (1H, s), 2.88, 2.55 (2H, AB quartet, $J =$ 17.7 Hz), 2.41 (3H, s), 2.19 (3H, s), 1.16 (3H, s), 1.01 (3H, s), $^{13}$C NMR (CDCl$_3$) δ 207.5, 137.2, 131.6, 131.1, 130.1, 128.3, 126.0, 121.0, 52.2, 40.8, 38.2, 31.9, 25.4, 23.2, 20.4, IR (CCl$_4$) 2362, 1714 cm$^{-1}$, EI Mass 43, 171, 186, 229 (M$^+$). The AB quartet of the geminal α -protons to the carbonyl group can be explained by an effect of the chiral center nearby.

**2-( *o*- tolyl)-3-methyl-2-butenenitrile.** After irradiation of OTCMP to complete conversion, the concentrated sample was chromatographed on silica gel using hexane and ethyl acetate (5 to 1) as eluents. The resulting compound was also compared with the authentic sample which was separately prepared by condensation of o-tolylacetonitrile and acetone. 1H NMR (CDCl$_3$) δ 7.25-7.07 (4H, m), 2.29 (3H, s), 2.25 (3H, s), 1.69 (3H, s), $^{13}$C NMR (CDCl$_3$) δ 155.4, 138.7, 133.4, 130.4, 129.7, 126.6, 126.1, 117.9, 109.9, 23.9, 21.1, 19.4, IR (CCl$_4$) 2210, 1446 cm$^{-1}$, EI Mass 156, 171 (M$^+$).

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# Zinc Acetate as a Catalyst for *Di*- and *Tri* imide Formation from 1,8-Naphthalic Anhydride and Aromatic Polyamides

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Six-membered naphthalic anhydrides are more stable and less reactive towards amine groups than their five membered ring counterparts.[1] There is a great range of reactivity for aromatic polyamides which depends on the spatial relationship between the various amine groups. For 1,4-diaminoarenes, imide formation at one amine can suppress reaction at the other amine.[2,3] This effect makes it dfficult to prepare six-membered aromatic diimides from 1,4-phenylenediamine. For example Hodgkin[2a] reported that the condensation of 1,8-napthalic anhydride (**4**) and 1,4-phenylenediamine (**3**) in DMSO or DMF at reflux give only *mono* imide while a 3 : 2 ratio of *mono* imide and *di* imide **1** was formed in DMAC at reflux for 24 hrs.

The condensation of bisanhydrides and aryl monoamine under $Zn(OAc)_2 \cdot 2H_2O$ catalysis has been used to prepare *mono* imides.[4] In this study, we use zinc acetate dihydrate as a catalyst to form the naphthalic *di* imide **1** and naphthalic triimide **2** (Figure 1).
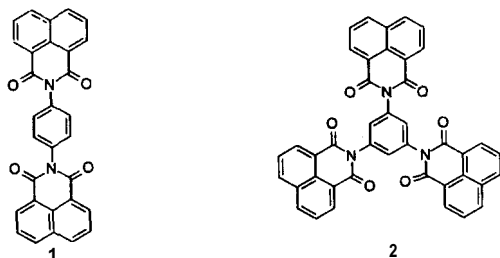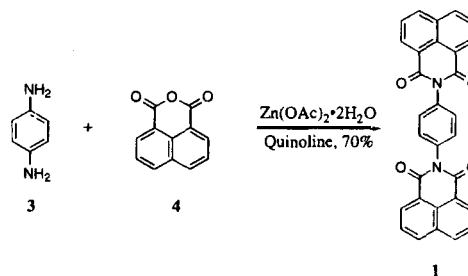


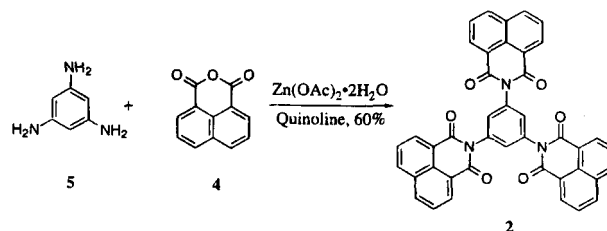**Figure 1.** Naphthalic Diimide **1** and Naphthalic Triimide **2**.

The six-membered aromatic *di* imide **1** was prepared from 1,4-phenylenediamine (**3**) and 1,8 naphthalic anhydride (**4**) in the presence of a catalytic amount (10 mol %) of Zn(OAX)$_2$· 2H$_2$O in quinoline (a 0.03 M solution) at 200 °C. In this reaction the *di* imide **1** was formed in 70% yield uncontaminated by *mono* imide (Scheme 1).

Alternatively, the aromatic *tri* imide **2** was synthesized from 1,3,5-phenylenetriamine (**5**) [5] and naphthalic anhydride (**4**) under similar conditions in 60% yield (Scheme 2).

In summary, we have shown that six-membered ring *di*-



**Scheme 1.**



**Scheme 2.**

imides and *tri* imides can be prepared using $Zn(OAc)_2 \cdot 2H_2O$ as a catalyst. We will apply this result to the preparation of polymeric versions of six-membered arylimides **1** and **2** form polyamine monomers **3** and **5.**

## Experimental

**General.** All commercial chemicals were used as obtained without further purification, and all solvents were carefully dried and distilled by standard methods prior to use. Column chromatography was carried out on silica gel 600 (E. Merk, 230-400 mesh) with the flash technique.[6] Nuclear magnetic resonance spectra were recorded on either WP-200 or AM-300 spectrometer, Chemical shifts are reported in δ ppm relative to (CH$_3$)$_x$Si for $^1$H NMR. Coupling constants, *J,* are reported in Hz. Infrared spectra (cm$^{-1}$) were obtained on a Perkin-Elmer 1600 FT infrared spectrometer. Positive fast atom bombardment mass spectra