

ed into a catalytic role, not only for reduction but for a wide variety of reactions. Application of this activated metal powder to the Simmons-Smith and Reformatsky reactions is currently under investigation.

Acknowledgement. We thank the Korea Science and Engineering Foundation for financial support.

References

1. A. Furst, *Chem. Rev.*, **65**, 51 (1965).

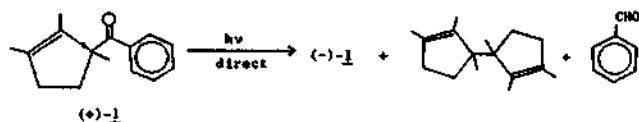
2. T. Hirashima and O. Manabe, *Chem. Lett.*, 259 (1975).
3. N. R. Ayyangar, U. R. Kalkote and K. V. Spinivasan, *Synthesis*, 938 (1984).
4. B. H. Han, D. H. Shin and S. Y. Cho, *Bull. Kor. Chem. Soc.*, 320 (1985).
5. N. R. Ayyangar, U. R. Kalkote and A. G. Lugade, *Bull. Chem. Soc. Jpn.*, **56**, 3159 (1983).
6. B. H. Han, D. H. Shin and S. Y. Cho, *Tetrahedron Lett.*, **26**, 50 6233 (1985).

Racemization vs. 1,3-Shift in the Excited State of 1-Methyl-2-Cyclohexenyl Phenyl Ketone

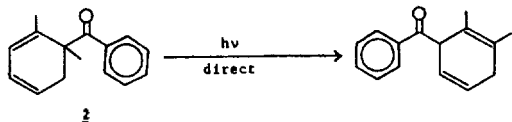
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The most β,γ -unsaturated ketones undergo 1,3-acyl migration under the direct irradiation and 1,2-acyl migration under the sensitized irradiation.¹ Schaffner² and coworkers have investigated the 3-benzoyl cyclopentene (**1**). Irradiation of optically active ketone **1** gave racemic mixture along with the α -cleavage, recombination products and benzaldehyde.

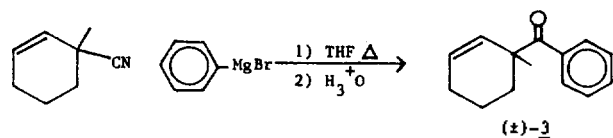


S. J. Lee³ have studied the photochemistry of benzoyl cyclohexadiene derivatives (**2**). The cyclic $\beta,\gamma,\delta,\epsilon$ -unsaturated ketone **2** are system in which 1,5-shift seems more likely. However, direct photolysis of **2** gave only the 1,3-shift product.



Since the bezoyl groups showed variety of photo-reaction depend upon the olefinic moiety, we have decided to investigate the migratory aptitude and the singlet-triplet reactivity of 1-methyl-2-cyclohexenyl phenyl ketone (**3**) which is analogous to the ketone **2**.

The ketone **3** chosen for study was synthesized by the Grignard reaction of 1-cyano-1-methyl-2-cyclohexene.⁴



Direct irradiation of ketone **3** in ether at 350 nm for 40 min showed no significant change in nmr spectrum and GC

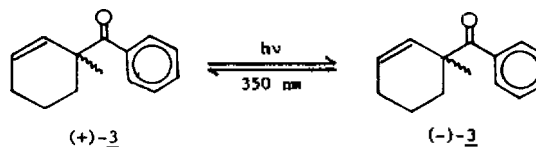
Table 1. Change in Optical Rotation During the Irradiation of (+) Ketone **3**

Time (min.)	Optical rotation, $[\alpha]$	$\ln[\alpha_0]/[\alpha_t]$
0	+36.474	0
5	+33.055	0.098
10	+30.775	0.170
20	+25.076	0.375
30	+21.657	0.521
40	+18.237	0.693

analysis. Nmr and GC analysis revealed that there were neither 1,3-shift nor decomposition during the 40 min irradiation. Over 60 min irradiation of ketone, however, produced products along with α -cleavage, recombination, and benzaldehyde.

The (\pm)-ketone **3** was resolved to see if the photo-racemization occurs under irradiation condition. The optical resolution of (\pm)-ketone **3** was performed by the selective ketalization⁵ of the ketone **3** with (2R, 3R)-2,3-butandiol and since the photo-racemization is first order kinetics, the optical purity and the absolute configurations were not determined.

Direct irradiation of the resolved ketone **3** at 350 nm showed racemization only and the quantum efficiency^{6,7} was calculated as 0.75 using the rate constant of first order kinetics, i.e. $\ln k = \frac{\alpha_0}{\alpha_t}$ where k 0.0171/min. (Table 1).



The photo-racemization of ketone **3** was quenched by the addition of trans-piperylene and linear Stern-Volmer relationships were observed as shown in Fig. 1.

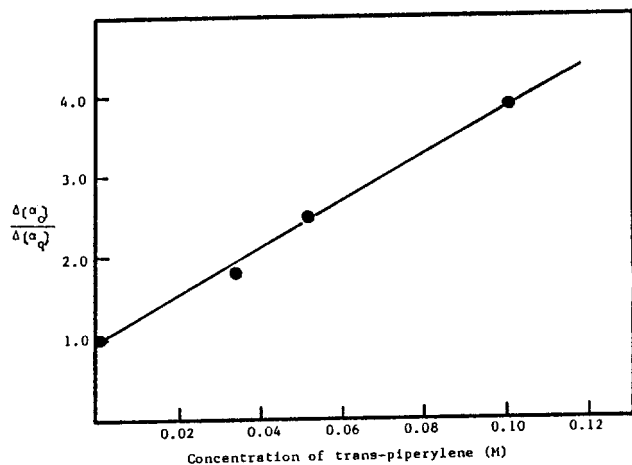
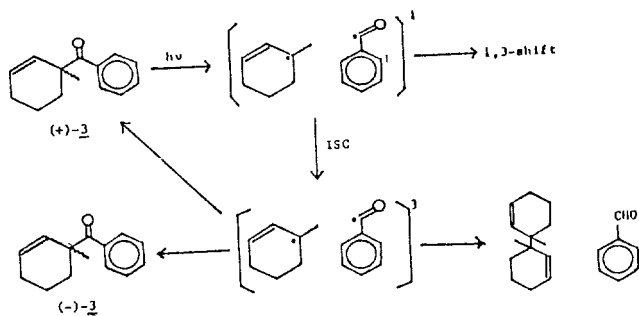


Figure 1. Stern-volmer quenching of the photo-racemization of (-)-ketone 3.

Based upon these facts, the racemization mechanism was suggested as follows:



The mechanism involves α -cleavage to yield alkyl and benzoyl radical, which recombine to afford racemization.

Since the efficient racemization was quenched and the fluorescence emission was not detected, an efficient intersystem crossing may prevent producing 1,3-shift product, which generally comes from singlet state. Ketone 3 is one of a few^{8,11} ketones which intersystem cross under the direct

irradiation condition. The direct vs. sensitized triplet state of ketone 3 including racemization, 1,3-shift and the oxa-di- π -methane (ODPM) rearrangement products are under investigation.

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References

1. K. N. Houk, *Chem. Rev.*, **76**, 1 (1976).
2. K. Shaffner, B. Blank, and H. Fischer, *Helv. Chim. Acta*, **56**, 1741 (1973).
3. A. S. Kende and S. J. Lee, Unpublished results; S. J. Lee, Ph.D. Thesis, University of Rochester, 1970.
4. R. S. Givens and Woo Ki Chae, *J. Kor. Chem. Soc.*, **26**, 99 (1982).
5. Resolution of the racemic ketone 3 was performed by the adaption of the procedure developed by K. Schaffner, *J. Am. Chem. Soc.*, **106**, 2064 (1984).
6. A solution of 329 mg (1.65 mmol) of (+)-3 in 15 ml of dried ether was degassed with purified nitrogen. Irradiation was carried out with 4 RPR-3500 Å lamps. Light output was monitored by potassium ferrioxalate actinometry according to the method of Hatchard and Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).
7. The efficiency of the photo-racemization was calculated by the equation^{a,c}, $\phi_{rac} = C_0/2mE \cdot kt$; (a) R. S. Givens and W. K. Chae, *J. Am. Chem. Soc.*, **100**, 6278 (1978); (b) R. S. Givens and W. K. Chae, *J. Am. Chem. Soc.*, **104**, 2456 (1982); (c) Woo Ki Chae, *J. Kor. Chem. Soc.*, **27**, 302 (1983).
8. P. S. Engel, M. A. Schexnayder, *J. Amer. Chem. Soc.*, **96**, 924 (1974).
9. P. S. Engel, *ibid.*, *Tetrahedron Lett.*, 1157 (1975).
10. S. D. Parker and N. A. J. Rogers, *Tetrahedron Lett.*, 4389, 4393 (1976).
11. J. C. Dalton, M. Shen and J. J. Snyder, *J. Am. Chem. Soc.*, **98**, 5023 (1976).

O-Debenzoylation and Methoxylation of Some Tribenzoylated Pyridazine Nucleosides

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In connection with our research for the synthesis of some biologically active pyridazine nucleosides, we have attempted the synthesis of some cyanopyridazine nucleosides from mono- or dichloropyridazine nucleosides with the fully benzoylated sugar moiety and KCN in methanol solvent. We have, however, obtained the corresponding mono- and dimethoxypyridazine nucleosides with the fully debenzoylated sugar moiety instead of cyanopyridazine nucleosides contain-

ing the protected sugar moiety. On the other hand, mono- or dicyanopyridazine nucleosides were synthesized from CuCN-DMSO system.¹

This preliminary result is interesting in nucleic acid chemistry. The deprotection of benzoyl or acyl groups on 2', 3' and 5'-positions of sugar moiety is one of the most important procedure in the field of sugar, nucleoside and nucleotide chemistry. In general, acyl groups of protected esters have