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Photo-induced Reactions. XIX. Photopinacolization of Unsymmetric Aromatic Ketones[1]

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Stereochemistry of the photopinacolization of unsymmetrical aromatic ketones was investigated. In the photopinacolization of aromatic ketones of type PhCOR in isopropyl alcohol, the *dl* : *meso* ratio of diastereoisomeric pinacols formed tends to increase as the size of the substituent R becomes bulkier. The *dl* : *meso* ratio of pinacols obtained from *p*-substituted acetophenone, *p*-X-C_6H_4-$COCH_3$, is about 1 in the cases that X is H, Cl, and CH_3, whereas the ratio is 1.25 in the case of X=OCH_3. The photopinacolization of acetophenone in three solvent systems cyclohexane, isopropyl alcohol, and benzene-isopropyl alcohol, was also investigated, and no solvent effect was observed on the *dl* : *meso* ratio of acetophenone pinacols.

The photoreduction of ketones, especially aromatic ketones, is one of the most extensively investigated field in organic photochemistry.[2] Unsymmetrical ketones, which can undergo photopinacolization, should give two diastereoisomeric pinacols, *dl* and *meso* forms. However, there have been only a few reports in which the ratio of such diastereoisomeric pinacols is described. It was reported that *o*-phenylbenzophenone[3] and desoxybenzoin[4] yield a higher melting pinacol predominantly over a lower melting isomer. Bencze and his coworkers found that 3-acetylpyridine yields a higher melting pinacol accompanying with a small amount of a lower melting one, while 2-acetylpyridine gives approximately an equal amount of two isomeric pinacols.[5] Brown reported that the photolysis of benzyl alcohol in acetone affords an equal amount of *dl*- and *meso*-hydrobenzoin.[6] Furthermore, acetophenone was shown to give corresponding pinacols with the *dl* : *meso* ratio of 11 : 10[7] Since there has been no systematic investigation on the

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[1] Part XVIII: T. Matsuura and K. Ogura, *Tetrahedron*, in press.

[2] For a review see, D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publ. Co., New York (1967), p. 163.

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[4] F. Bergmann and Y. Hirschberg, *J. Am. Chem. Soc.*, **65**, 1429 (1943).

[5] W. L. Bencze, C. A. Burkhardt and W. L. Yost, *J. Org. Chem.*, **27**, 2865 (1962).

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[7] J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **31**, 3755 (1966).

TABME 1. PHOTOPINACOLS III FROM ALKYL PHENYL KETONE I

$$\underset{\text{(I)}}{C_6H_5COR} \longrightarrow \underset{\text{(III)}}{(C_6H_5C(OH)R)_2}$$

R	Yield of III (%)	Chemical shifts of R-protons of III[a] (τ value)		*dl*: *meso* ratio
		dl	*meso*	
H	70	H: 5.31 s	H: 5.18 s	0.9
CH_3	80	CH_3: 8.55 s	CH_3: 8.47 s	1.0
C_2H_5	75	CH_3: 9.40 t CH_2: 8.30 q, 7.86 q	CH_3: 9.40 t CH_2: 8.40 q, 7.60 q	1.0
i-C_3H_7	55	CH_3: 9.66 d, 8.79 d CH: 8.02 sep	CH_2: 9.36 d, 9.26 d CH: 7.81 sep	1.1_8

a) The spectra were taken in $CDCl_3$. Multiplicities of signals are shown as follows: s, singlet; d, doublet; t, triplet; q, quartet; sep, septet.

stereochemistry of the photopinacolization of unsymmetric aromatic ketones, we initiated to examine effects of substituents and solvents in this reaction. Particular attention was drawn to following three factors; namely, (i) effects of the bulkiness of the substituents R in ketones of type PhCOR, (ii) electronic effects of the para substituent in *p*-substituted acetophenone, and (iii) solvent effects with acetophenone.

A mixture of diastereoisomeric pinacols could be easily separated by a column chromatography on silica gel from the reaction mixture which was obtained by the photolysis of PhCOR (I) and *p*-X-C_6H_4-$COCH_3$ (II) in isopropyl alcohol. The *dl* : *meso* ratio of these diastereoisomeric pinacols was determined from their peak areas in the NMR spectrum of the pinacol mixture. The results are shown in Tables 1 and 2. In the case of pinacols III obtained from I, the chemical shifts of protons of the substituent R are different between *dl* and *meso* forms, and the signals of the *dl* form appear in a higher field than those of the *meso* form. The assignment of the signals was accomplished by a comparison with authentic samples.*1 The authentic sample of *dl*-hydrobenzoin (III, R=H) was prepared by a known method, and other authentic samples of the pinacols III (R=CH_3, C_2H_5, and *i*-C_3H_7) were obtained by fractional recrystallization of the pinacol mixture and they were characterized by a comparison of their melting points with those reported in the literature. In the case of pinacols III (R=*i*-C_3H_7), the *dl* and *meso* forms were characterized, from their infrared spectra, according to the method of Mosher and Heindel.10) A mixture of the *dl* and *meso* pinacols of type IV was also separated from the reaction mixture, but each isomer was not isolated. For these pinacols, an isomer showing a methyl signal in a higher magnetic field was assigned as the *dl* form and in a lower field as the *meso* form.8)

TABLE 2. PHOTOPINACOLS IV FROM *p*-SUBSTITUTED ACETOPHENONE II

$$\underset{\text{(II)}}{p\text{-X-}C_6H_4COCH_3} \longrightarrow \underset{\text{(IV)}}{(p\text{-X-}C_6H_4C(OH)CH_3)_2}$$

X	Yield of IV (%)	Chemical shifts of aliphatic methyl protons of IV (τ value)		*dl*:*meso* ratio
		dl	*meso*	
H	80	8.55	8.47	1.0
CH_3	85	8.63	8.53	1.0
Cl	88	8.60	8.52	1.0
CH_3O	90	8.60	8.50	1.2_5

As shown in Table 1, the *dl* : *meso* ratio of the pinacols III obtained from I appears to have a tendency to increase slightly as the size of the substituent R becomes bulkier. Contrary to the recent results by Stocker and Kern,7) our results indicate that the *dl* : *meso* ratio is practically 1 : 1 for R=CH_3 and C_2H_5. Although we also examined the photopinacolization of *n*-butyrophenone (I, R=*n*-C_3H_7) and *t*-butyl phenyl ketone (I, R=*t*-C_4H_9) in isopropyl alcohol, photopinacolization was found to be a minor pathway and the yield of the pinacols were so low that the *dl* : *meso* ratio could not be determined. It was found that the former undergoes the Norrish Type I process whereas the latter does the Type II process as the major pathway. The somewhat lower yield of the pinacols III (R=*i*-C_3H_7) is probably due to the co-occurrence of the Type I process in some extent.

Table 2 summarizes the effect of the *p*-substituent of acetophenone on the *dl* : *meso* ratio of pinacols

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*1 The NMR data of acetophenone pinacols9) and propiophenone pinacols9) have been reported.

8) H. Agahigian, J. F. Maraveck and H. Gauther, *Can. J. Chem.*, **41**, 194 (1963).

9) H. D. Becker, *J. Org. Chem.*, **32**, 2143 (1967).

10) W. A. Mosher and N. D. Heindel, *ibid.*, **28**, 2154 (1963).

IV. The *dl* and *meso* isomers are formed practically in an equal amount in the cases of X=H, CH$_3$, and Cl. On the other hand, the *dl* isomer is formed predominantly over the *meso* isomer when X is a methoxyl group, a strong electron-donating group. Similarly, *p*-anisaldehyde gives a mixture of the *dl* and *meso* pinacols with 2 : 1 ratio.[11] Analogous observation has been reported by Pitts and his coworkers[12] who show that, in the Norrish Type II reaction of *n*-butyrophenone, the quantum yield is remarkably affected by introducing a *p*-methoxyl group while a *p*-methyl group has little effect.

It was reported that, in the photopinacolization of acetophenone, there is no solvent effect on the *dl* : *meso* ratio of its pinacols formed in isoproyl alcohol or cyclohexane.[12] We also carried out the photopinacolization of acetophenone in three solvent systems and similar results were obtained. A mixture of two diastereoisomeric pinacols was obtained in 80% yield in isopropyl alcohol, 87.5% in 50 : 1 benzene-isopropyl alcohol, and 68% in cyclohexane. In all cases, the *dl* : *meso* ratio was found to be 1 : 1 within experimental errors.

From the above results, it appears that there are at least two factors, which influence the *dl* : *meso* ratio of photopinacols, namely steric and electronic effects of the substituent. Further examples and mechanistic consideration will be reported in a future paper. After completion of this work, Stocker and his coworkers have reported that *p*-substitution of acetophenone with an electron-donating group results in the predominant formation of the *dl* pinacol over *meso* pinacol,[13] and that, in the photopinacolization of acetophenone, neutral organic solvents do not change appreciately the *dl* : *meso* ratio.[14] These results are essentially same as our results.

Experimental

Materials. The starting materials were commercially available. Their purities were checked by gas chromatography. The solvents, isopropyl alcohol, cyclohexane, and benzene, were dried and distilled before use. *dl*-Hydrobenzoin was prepared from *trans*-stilbene by a known method,[15] mp 123—125°C.

General Procedure for Photopinacolization. The following procedure was used for experiments of Table 1. A solution of 2.00 g of the starting aromatic ketones in 200 m*l* of isopropyl alcohol was irradiated under nitrogen at room temperature using a 100 W high-pressure mercury lamp (Ushio, UM 100) with a water-cooled Pyrex jacket. After the starting material had been consumed (6—9 hr), the mixture was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column. Elution with chloroform yielded a mixture of *dl*- and *meso*-pinacols. The *dl* : *meso* ratio of the mixture was determined by NMR analysis. The results are summarized in Table 1. In the case of isobutyrophenone, 2.00 g of the ketone was dissolved in 350 m*l* of isopropyl alcohol and the solution was irradiated using a 450 W high-pressure mercury lamp (Ushio, UM 450).

For experiments of Table 2, 1.10 g of *p*-methylacetophenone, 1.00 g of *p*-methoxyacetophenone, and 0.55 g of *p*-chloroacetophenone were dissolved in 300 m*l* of isopropyl alcohol, respectively. Each solution was irradiated by a 450 W lamp for 7—8 hr as described above.

For experiments in different solvent systems, the following solution was irradiated by a 450 W lamp: 0.50 g of acetophenone in 350 m*l* of cyclohexane (12 hr) and 2.00 g of acetophenone in 500 m*l* of benzene containing 10 m*l* of isopropyl alcohol (19.5 hr).

Isolation and Characterization of Diastereoisomeric Pinacols. Some of the diastereoisomeric pinacols were separated by fractional recrystallization (*n*-hexane or petroleum ether) from the pinacol mixtures obtained as above. The melting points of pinacols isolated are listed below: *dl*-acetophonone-phinacol, 124—125°C (lit.[10] 122—123°C); *meso*-acetophenonepinacol, 119—120°C (lit.[10] 117—118°C); *dl*-hydrobenzoin, 123—125°C (lit.[16] 120°C); *meso*-hydrobenzoin, 137°C (lit.[17] 137°C); *dl*-propiophenonepinacol, 113—114°C (lit.[10] 113°C); *meso*-propiophenonepinacol, 140—141°C (lit.[10] 138—139°C); *dl*-isobutyrophenonepinacol, 159°C; *meso*-isobutyrophenone-pinacol, 130—133°C. Stereochemistry of the latter two pinacols was assigned by infrared spectroscopy[10]: $\nu_{max}^{CCl_4}$ 3568 (strong), 3612 (medium), 1150, and 1177 cm^{-1} for the *dl*-isomer and 3574 (weak) 3614 (strong), and 1121 cm^{-1} for the *meso*-isomer. Other diastereoisomeric pinacols were not separated.

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[11] Unpublished data from this laboratory.

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