Quantitative Studies in Stereochemistry. Photochemistry. IV. The Ratios of Diastereomeric Pinacols Formed in the Ultraviolet-Promoted Bimolecular Reduction of Acetophenone-[7-^{14}C] in Amine Media

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Previous reports from this laboratory have dealt with the stereochemical consequences of photopinacolizing acetophenone or benzaldehyde in neutral–acidic[1a] and in strongly alkaline media,[1b] as well as the results from a number of *para*-substituted acetophenones.[1c] The present note further extends the study to an examination of the ratios of *dl*- to *meso*-acetophenone pinacols observed when amines are employed as the solvent/donor.

The use of amines in the photopinacolization of benzophenones has been examined by Cohen and coworkers,[2] and by Davidson.[3] These investigators established that amines can serve as hydrogen donors, occasionally more satisfactorily than their carbinol counterparts. The present study would appear to be the first to examine acetophenone for corresponding reactivity. This was deemed desirable in view of the fact that acetophenone and benzophenone display strikingly different chemical behavior upon irradiation in strongly alkaline media.[1b] This is also the first report concerning the effects of amines upon the ratio of diastereomers produced in a reaction of this type.

Five amines, selected for their diversity, were utilized in isotope dilution experiments. The results are tabulated in Table I. All amines examined proved to be satisfactory hydrogen donors but inferior to 2-propanol in this respect. Certain selected values from earlier studies in other solvent/donors are included in the table for evaluative comparisons.

Table I

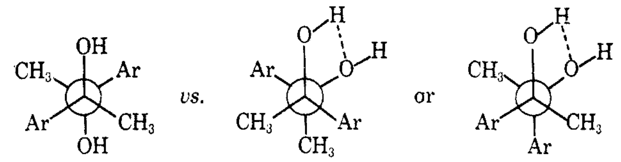
Photopinacolization of Acetophenone-[7-^{14}C]

Run	Solvent/donor	Time, hr	Pinacol yield,[a] %	Ratio *dl*/*meso*
1[b]	2-Propanol (0.01 *N* potassium 2-propoxide)	18	56.4	2.98
2[b]	50% aqueous 2-propanol	18	94.6	1.31
3[c]	2-Propanol	18	100	1.09
4[b]	Cyclohexane	72	33.5	1.03
5	Tri-*n*-propylamine	42	58.4	1.02
6	Piperidine	18	81.9	0.95
7	Di-*n*-butylamine	42	82.1	0.93
8	Isopropyl amine	18	79.6	0.90
9	DABCO[d]	42	21.4	0.81

[a] Based on starting ketone. [b] From ref 1b. [c] From ref 1a. [d] Diazabicyclooctane (triethylenediamine), 5 g in 15 ml of C_6H_6.

An explanation of the stereochemistry observed in alcoholic media has been previously proposed.[4] It was suggested that interspecies hydrogen bonding between radicals about to dimerize, in competition with simple steric control, played a role in determining the resultant ratio of diastereomeric pinacols as illustrated in Scheme I.

Scheme I



meso
Simple steric control

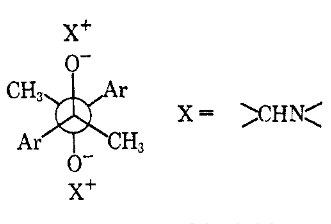
dl
Hydrogen bonding control

The stereochemistry observed with the use of amines cannot be due to the basicity of the amines, since alkaline solutions increase the *dl* to *meso* ratio (run 1).[4] Similarly, a consideration of solvent polarity will not account for the data. Solvents ranging from cyclohexane to aqueous alcohol all yield the *dl*-pinacol as the preponderant diastereomer (runs 2, 3, 4). The *meso*-pinacol predominates only in amine solution.

This anomalous behavior in the presence of amines may be ascribable to a difference in the mode of hydrogen transfer. It has been established that in alcoholic media a hydrogen atom is abstracted from the carbinol donor by the triplet ketone.[5] Cohen,[2a] however, has suggested that the corresponding amine reactions may proceed by an initial electron transfer from the nitrogen atom of the amine to the triplet ketone, with a subsequent proton transfer and electron redistribution, according to the sequence

$$>\mathrm{CH}\ddot{\mathrm{N}}< + \overset{*}{\mathrm{O}}{=}\mathrm{C}< \longrightarrow >\mathrm{CH}\underset{+}{\dot{\mathrm{N}}}< + \underset{-}{\mathrm{O}}{-}\dot{\mathrm{C}}< \longrightarrow$$
$$>\dot{\mathrm{C}}{-}\ddot{\mathrm{N}}< + \mathrm{HO}{-}\dot{\mathrm{C}}<$$

We would like to suggest that if the polar intermediates above exist in the form of an ion pair and are sufficiently long lived, dimerization may take place between two such species. Hydrogen bonding during the dimerization step would not be expected to play a significant role in this case. The sterically most favorable resulting structure would then be



Protonation of the above would yield the *meso*-pinacol. A relatively small contribution from this pathway would account for the lower *dl*/*meso* ratios observed when amines are used as solvent/donors.

From the limited number of amines examined, there would appear to be a qualitative correlation between the base strength and steric availability of the electron pair, and the observed stereochemistry.

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[1] (a) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **31**, 3755 (1966); (b) J. H. Stocker and D. H. Kern, *ibid.*, **33**, 291 (1968); (c) J. H. Stocker, D. H. Kern, and R. Jenevein, *ibid.*, **33**, 412 (1968).

[2] (a) S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, **89**, 164 (1967); (b) S. G. Cohen and R. J. Baumgarten, *ibid.*, **87**, 2996 (1965).

[3] R. S. Davidson, *Chem. Commun.*, 575 (1966).

[4] For a detailed discussion of the photopinacolization of acetophenone in acidic and basic media, see ref 1b.

[5] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Amer. Chem. Soc.*, **81**, 1068 (1959).

Experimental Section

The source or synthesis of the acetophenone-[7-^{14}C], *meso*- and *dl*-acetophenone pinacols, as well as the apparatus and general procedure employed, has been previously described.[1a,b] The several amines examined were of the highest research grades obtainable and further purified by traditional techniques where deemed necessary. All reaction mixtures involved 1 g of ketone and 10 ml of amine excepting run 9 as noted in the Table I compilation footnotes.

Registry No.—Acetophenone-[7-^{14}C], 5821-66-9.

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Quantitative Studies in Stereochemistry. Photochemistry. V. The Ratio of Diastereomeric Pinacols Formed in the Ultraviolet-Promoted Bimolecular Reduction of Deoxybenzoin

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As part of a broad program designed to study the stereochemistry of the photopinacolization process, reports from this laboratory have described the ratio of diastereomeric pinacols formed from acetophenone[1,2] and various *para*-substituted acetophenones.[3] The present report describes a quantitative measurement by nmr techniques of the amounts of the two pinacols formed when an α-substituted acetophenone, deoxybenzoin, is photopinacolized in 2-propanol in both acidic and basic media. Formal assignment of diastereomeric identity of the pinacols is also made.

In compiling all pertinent literature data, it was noted that previous reports of the predominant diastereomer formed when deoxybenzoin was photopinacolized were in conflict with each other. Thus, Bergmann and Hershberg[4] reported obtaining the higher melting α pinacol (mp 214°) in 80% yield; "no trace of the β form was detected." On the other hand, Crawford and coworkers[5] have reported a 97% yield of a pinacol with a melting point of 172°, corresponding to the lower melting β isomer.[6] By implication, each of the above reactions proceeded in a highly stereoselective manner but with stereochemically different results.

The pure pinacols utilized in the present study were synthesized photochemically. The nmr of each showed a quartet for the nonequivalent benzylic protons, an hydroxylic proton, and a complex phenyl signal. The spectra were sufficiently different so as to provide a convenient means of distinguishing the two pinacols, independently and in mixtures. Consequently, the crude reaction mixture was analyzed by nmr, and the amounts of each isomer as well as residual ketone were obtained. In neutral or slightly acidic 2-propanol, high yields of 1,2,3,4 tetraphenyl-2,3-butanediol result. From 0.5 g of deoxybenzoin, an 82% yield of pinacol was obtained with 16% unreacted starting material after 4 hr of irradiation. From 1.0 g of deoxybenzoin, a quantitative yield of pinacol was obtained after 12 hr. The ratio of β-to α-pinacol was 1.15 ± 0.05. In basic solution, 0.5 g of ketone yielded 75% pinacol after 12 hr, with 22% recovered deoxybenzoin, and a β to α ratio of 3.0 ± 0.1.

By analogy to a number of other pinacols, the *meso* structure was assigned to the diastereomer with the hydroxylic proton at higher field strength[7] (α-pinacol). Correspondingly, the β-pinacol is the *dl* isomer. Thus, the *dl*-pinacol predominates in both acidic and basic 2-propanol. These results are analogous to those obtained for acetophenone, which yields *dl* to *meso* ratios of 1.10 and 2.85 in acid and base, respectively.[2]

It must be concluded that both of the previous reports[4,5] are incorrect and the reaction proceeds, as do the comparable acetophenone photopinacolizations, with a rather low stereoselectivity.

Experimental Section

Deoxybenzoin, mp 54–56°, was obtained from Matheson Coleman and Bell and used as received. The 2-propanol was standard reagent grade and used without further purification. The general procedure[3] and photochemical apparatus[1] have been described; F8T5(BLB) bulbs (3500 Å peak) and Pyrex glass were used exclusively. All runs were made with a ketone concentration of 5%. The alkaline solutions were 50% aqueous 2-propanol, 0.2 *N* with respect to KOH. Melting points were determined on a Kofler hot stage and are uncorrected.

***meso*-1,2,3,4-Tetraphenyl-2,3-butanediol (α-Pinacol).**—The suspension resulting from the irradiation of 1 g of deoxybenzoin in acidic 2-propanol was filtered, and the white needles were recrystallized from heptane to yield 380 mg of pinacol: mp 213–214°; nmr, phenyl, τ 2.80 (multiplet, 20 H); benzylic, 6.68 (quartet, 4 H), $J_{AB} = 14$ cps, $\Delta\nu_{AB} = 43$ cps; hydroxylic, 7.90 (singlet, 2 H).

***dl*-1,2,3,4-Tetraphenyl-2,3-butanediol (α-Pinacol).**—The mother liquor from the above was concentrated and crystallized from heptane to yield 350 mg of pinacol: mp 171–172°; nmr, phenyl, τ 2.80 (multiplet, 20 H); benzylic, 6.75 (quartet, 4 H), $J_{AB} = 14$ cps, $\Delta\nu_{AB} = 28$ cps; hydroxylic, 7.51 (singlet, 2 H).

Registry No.—Deoxybenzoin, 451-40-1.

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

(2) J. H. Stocker and D. H. Kern, *ibid.*, **33**, 291 (1968).

(3) J. H. Stocker, D. H. Kern, and R. M. Jenevein, *ibid.*, **33**, 412 (1968).

(4) F. Bermann and Y. Hirshberg, *J. Amer. Chem. Soc.*, **65**, 1429 (1943).

(5) H. M. Crawford, M. E. Seager, and F. E. Warneke, *ibid.*, **64**, 2862 (1942).

(6) The two diastereomers of deoxybenzoin pinacol, 1,2,3,4-tetraphenyl-2,3-butanediol, are both known and have most frequently been prepared by the Grignard reaction or by the reduction of deoxybenzoin, or benzoin. E. J. Chu and J. Chu [*J. Chin. Chem. Soc.* (Taipei), **10**, 14 (1943)] record several pertinent references; they observed a melting point of 208–209° for the α and 172° for the β pinacol. Beilsteins Handbuch, [F. Richer, Ed., (Vol. VI, 4th ed, 2nd Suppl., Springer-Verlag, Berlin, 1944, p 1059)] lists 215–216° and 172–173° for the α and β forms, respectively. The corresponding figures from the present study (see Experimental Section) are 213–214° and 171–172°.

(7) This method of assignment has been previously employed: J. H. Stocker, *J. Amer. Chem. Soc.*, **88**, 2878 (1966). See also ref 3.