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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[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.