and triethylamine in ether[8] at −30° for 2 hr. In the first of these experiments a complex which had no ketene band at 4.8 μ was obtained in solution. However, on concentration or warming an exothermic reaction occurred and I was recovered. In one attempt to generate a sulfene[9] in the presence of I, no addition was obtained and 67% of the starting I was recovered. Similarly, 80% of I was recovered from an attempt at reaction of dimethylsulfoxonium methylide[10] with I. When benzyne was generated[11] in the presence of I the latter was recovered in 87% yield. Finally, no reaction occurred when a solution of diazomethane in methylene chloride[12] was added to I at 0° and the solution later allowed to come to room temperature. Catalysis of this reaction by cuprous chloride[13] was also ineffective.

On addition of gaseous formaldehyde to an ether solution of I containing catalytic amounts of boron trifluoride α,α-di-*t*-butyl-β-propiolactone (II) was formed in 68% yield. However, attempts to condense acetaldehyde or acetone under similar conditions afforded only di-*t*-butylacetic acid. The latter probably resulted from the reaction of water, formed in the aldol reactions of acetaldehyde and of acetone, with I.

All attempts to reduce II with sodium, zinc in formic acid, or with isoproplymagnesium iodide resulted in recovery of II. However, treatment with lithium aluminum hydride resulted in the formation of methyldi-*t*-butylacetic acid in 70% yield. This reduction of the carbon–oxygen single bond in II stands in marked contrast to the reduction of tetramethyl-β-propiolactone[14] and of α,α-diphenyl-β-propiolactone[15] to 1,3-propanediols.

Experimental Section

α,α-Di-*t*-Butyl-β-propiolactone (II).—To a magnetically stirred solution of 4.8 g of I in 20 ml of dry ether containing a few drops of BF_3–etherate in a 100-ml flask was passed the formaldehyde generated by heating 4.5 g of paraformaldehyde (dried for 2 weeks over P_2O_5) during 1 hr. After stirring for an additional 1.5 hr at room temperature the mixture was filtered to remove solids and the filtrate was added to water. The ether layer obtained by extraction was dried over $MgSO_4$ and the ether was removed by evaporation. Crystallization of the residue from hexane at −70° yielded 3.9 g (68%) of colorless II, mp 116–118°. The analytical sample (mp 118–119°) was obtained by sublimation and showed a strong absorption at 5.51 μ (1815 cm^{-1}).[16] The nmr spectrum showed a singlet (9 H) at τ 8.82 and a singlet (1 H) at τ 5.98.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.7; H, 10.9. Found:[17] C, 71.8; H, 11.1.

Methyldi-*t*-butylacetic Acid.—A solution of 1.84 g of II and 0.6 g of $LiAlH_4$ in 30 ml of THF was refluxed for 16 hr. After the usual isolation procedure 1.48 g of crude acid was obtained. Recrystallization from methanol–water gave 1.3 g (70%) of pure acid, mp 179–180°.

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.9; H, 11.9. Found:[17] C, 71.1; H, 12.0.

The nmr spectrum in CCl_4 showed two singlets at τ 8.86 and 8.81 in the ratio of about 5.8:1 (there was some difficulty in integration owing to the proximity of the peaks[18]).

Registry No.—Methyl-di-*t*-butylacetic acid, 16021-12-8; II, 16021-13-9.

---

(8) J. S. Swenson and D. J. Renaud [*J. Amer. Chem. Soc.*, **87**, 1394 (1965)] generated dicyanocarbene in this way.

(9) W. E. Truce and J. R. Norell, *ibid.*, **85**, 3231 (1963).

(10) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

(11) G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).

(12) W. B. Hammond and N. J. Turro, *ibid.*, **88**, 3672 (1966).

(13) W. von E. Doering and W. Roth, *Tetrahedron*, **19**, 715 (1963).

(14) G. Natta, G. Mazzanti, G. Pregaglia and M. Binaghi, *J. Amer. Chem. Soc.*, **82**, 5511 (1960).

(15) H. E. Zautgg and B. W. Horrom, *Anal. Chem.*, **20**, 1026 (1948).

(16) Y. Etienne and N. Fischer, "Heterocyclic Compounds with Three- and Four-membered Rings," part II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 779.

(17) Microanalyses by Galbraith Laboratories, Inc., Knoxville, Tenn.

(18) We thank Professor Robert Ouellette for this determination.

Quantitative Studies in Stereochemistry. Electrochemistry. II. The Ratio of Diastereomeric Glycols Formed in the Electrolytic Bimolecular Reduction of Benzaldehyde and Propiophenone

JACK H. STOCKER AND ROY M. JENEVEIN

Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122

Received September 27, 1967

Previously reported[1] isotope dilution studies in the title area described the ratios of *dl*- to *meso*-acetophenone pinacol observed in acid and alkaline media. A mechanism to account for the change from a ratio of approximately 1.2 *dl/meso* in acid media to 2.7–3.2 in alkaline media was proposed. The present note extends these studies to include the corresponding ratios resulting from the electrolytic reduction of carbon-14-labeled benzaldehyde and propiophenone. The two pairs of diastereomeric glycols needed for the dilution studies are known and their stereochemical identities were previously established.[2]

When the study was essentially complete, it was observed that adequately quantitative data could also be determined for the benzaldehyde system by nmr techniques.[3] Several such runs are included with the isotope dilution studies tabulated in Table I. Two new acetophenone runs by this technique, complementing those previously reported, are also included for useful comparisons.

With the exception of the results for the benzaldehyde system in alkaline media, the ratios show very little change from those observed when acetophenone is electrolytically reduced. In acid media, the reaction is slightly stereoselective in favor of the *dl* form for all three carbonyl compounds. There would appear to be a very slight increase in *dl/meso* ratio in the order benzaldehyde-acetophenone-propiophenone. The increase, if real, is very small.

The *dl/meso* ratios of pinacols formed in alkaline media fall in essentially the same range for acetophenone and propiophenone, 2.7–3.2. However, those for benzaldehyde drop sharply to an average of 1.2, unchanged from acid solution. Two possible explanations of the phenomenon can be made: (a) the

---

(1) J. H. Stocker and R. M. Jenevein, *J. Org. Chem.*, **33**, 294 (1968).

(2) For the assignment of diastereomeric hydrobenzoins, see G. Berti and F. Battari, *ibid.*, **25**, 1286 (1960). For the propiophenone pinacols, see W. A. Mosher and N. D. Heindel, *ibid.*, **28**, 2154 (1963).

(3) The relative heights of the *meso*- and *dl*-hydrohenzoin benzylic proton peaks provided the desired ratio; an area comparison with the total aromatic protons, after normalization, permitted yield calculations. Unreacted benzaldehyde may be determined from the aldehydic proton area. For analogous studies with substituted acetophenones, see J. H. Stocker, D. H. Kern, and R. M. Jenevein, *ibid.*, **33**, 412 (1968).

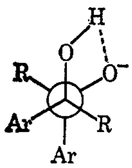
TABLE I

ELECTROLYTIC REDUCTION OF C_6H_5COR

Run	Electrode	Time, hr	Cathode potential (V)/ current (mA)	Medium[a,b]	Yield, % *dl*	Yield, % *meso*	Ratio *dl/meso*
			Benzaldehyde (R = H)				
1	Hg	20	−1.2/260	Acidic (A)	36.3	32.4	1.12
2	Hg	20	−1.6/290	Basic (B)	45.6	38.3	1.18
3[c]	Hg	15	−1.4/200	Basic (B)	45.5	41.0	1.11
4	Hg	1	−1.6/490	Basic (C)	48.9	37.5	1.30
5[c]	Hg	1	−1.6/500	Basic (D)	43.7	36.8	1.19
6	Cu[e]	20	−1.6/300	Basic (B)	39.1	33.7	1.16
7[c,d]	Hg	8	−/200	Basic (D)	96.5	<0.2	...
			Acetophenone (R = CH_3)				
8[c]	Hg	4	−1.2/450	Acidic (A)	39.9	31.3	1.27
9[c]	Hg	4	−1.2/200	Acidic (A)	43.4	34.6	1.25
			Propiophenone (R = C_2H_5)				
10	Hg	5	−1.2/300	Acidic (A)	31.3	22.3	1.40
11	Hg	7	−1.2/300	Acidic (A)	32.6	23.0	1.41
12	Hg	3.5	−1.6/300	Basic B	36.4	13.4	2.72
13	Hg	3	−1.6/450	Basic C	29.8	11.0	2.70
14	Hg	6.5	−1.6/300	Basic D	38.2	13.7	2.78
15	Cu[e]	4.5	−1.7/120	Basic B	18.0	5.5	3.25

[a] 80% EtOH in all cases. [b] (A) 1.7 *M* AcOH, 1.0 *M* LiCl; (B) 2 *M* KOAc; (C) 0.5 *M* Me_4NOH, 0.5 *M* Me_4NCl; and (D) 0.1 *M* KOH. [c] Nmr. [d] Stability study, pure racemate form used. [e] Smooth copper sheet, washed with dilute HNO_3 and rinsed thoroughly.

dimerizing phenyl hydroxymethyl radicals are sufficiently more reactive than the ketone-derived counterparts that the coupling process is less influenced by steric factors and generally less selective, or (b) the steric requirements of hydrogen are sufficiently less demanding than those of methyl or ethyl (see R in Table I) so as to limit the effectiveness of the following conformation (occuring at the time of dimerization)



in determining the resultant *dl/meso* ratio.[4] The present data is insufficient to choose between the two explanations at this time.

It may also be noted briefly that, as in the previously reported data for the acetophenone system, variations in time, current level, electrolyte, and choice of electrode did not make a significant contribution to the stereochemistry. The diastereomeric ratios appear to depend predominantly, if not exclusively, on the pH of the media.

Experimental Section

The purchase and purification, or preparation, of benzaldehyde-7-C^{14} and *meso*- and *dl*-hydrobenzoin have been previously described.[5] Propiophenone-7-C^{14} was purchased from Nuclear Research Chemicals, Orlando, Fla. *meso*- and *dl*-3,4-diphenyl-2,3-hexanediol were synthesized photochemically from propiophenone by standard techniques.

The general procedure has been reported in detail.[1] All runs contained 1 g of aldehyde or ketone in 60 ml of solution. In the isotope dilution studies, *meso*-hydrobenzoin was recrystallized to a final melting point of 136°, the *dl* form to 120°. For the propiophenone pinacols, the *meso* form was recrystallized to a melting point of 138° and the *dl* form to 86 or 114°.[6]

For nmr analyses, the basic media were first acidified with glacial acetic acid, and all reaction mixtures were quantitatively transferred with methanol. Following elimination of all alcohol on a rotary evaporator, the residue was extracted with dichloromethane (five 35-ml portions), the extract dried over anhydrous magnesium sulfate, and concentrated in an air stream on a steam bath. Carbon tetrachloride was added and concentration was continued to the exclusion of dichloromethane and essentially all of the tetrachloride. The nmr studies were conducted in deuteriochloroform. Nmr assignments for acetophenone pinacols have been reported;[3] for the hydrobenzoins, the *meso*-benzylic protons appear at 5.18 (2 H) and the *dl* at 5.32 (2 H).

Registry No.—Benzaldehyde, 100-52-7; propiophenone, 93-55-0; *meso*-hydrobenzoin, 579-43-1; *dl*-hydrobenzoin, 655-48-1; *meso*-pinacol of propiophenone, 16020-86-3; *dl*-pinacol of propiophenone, 16020-87-4.

Acknowledgment.—Financial assistance from the U. S. Atomic Energy Commission under Contract No. At-(40-1)-2833 (ORD-2833-19) is gratefully acknowledged. The nmr instrument utilized, an A-60 (Varian Corp.), was awarded Louisiana State University in New Orleans by the National Science Foundation under GP-3674.

---

[4] In paper I of this series[1] it was proposed that the stereochemistry was determined by the characteristics of dimerizing free radicals in acid media and coupling between radicals and radical ions in alkaline media. The paper may be consulted for fuller details.

[5] J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **33**, 291 (1968).

[6] The *dl*-pinacol is apparently polymorphic and the higher melting point is observed only with slow and particularly careful recrystallization.

The Acid-Catalyzed Dehydration–Condensation of 1,4-Cyclohexanediol[1a]

LEONARD H. SCHWARTZ, SHEILA B. AUSTER,[1b]
AND KENNETH KAUFMANN[1b]

Department of Chemistry,
The City College of The City University of New York,
New York, New York 10031

Received November 20, 1967

The dehydration of a mixture of the *cis* and *trans* isomers of 1,4-cyclohexanediol (quinitol) with aqueous

---

[1] (a) Support of this work by the National Science Foundation and the General Faculty Research Committee of The City College of New York is gratefully acknowledged. (b) National Science Foundation Undergraduate Research Participant.