

# The Synthesis of Glycols by Mercury-Photosensitized Alcohol Dehydrodimerization

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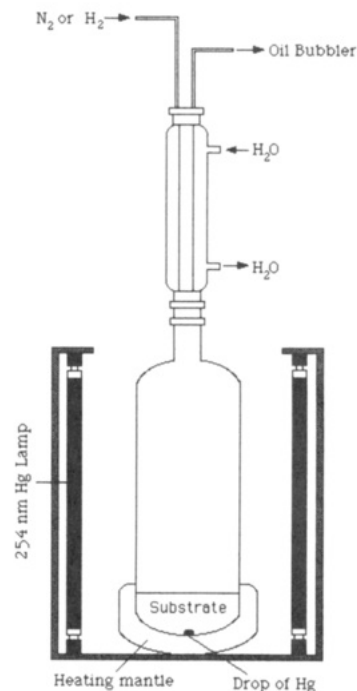
Received February 5, 1993

A variety of alcohols can be dehydrodimerized to give 1,2-diols on a multigram scale at 1 atm pressure and reflux temperature on photolysis (254 nm) in the presence of a trace of Hg vapor. Initial C–H bond breaking is followed by recombination of the resulting  $\alpha$ -C-centered radicals, which normally leads to C–C bond formation  $\alpha$  to oxygen. The reaction rate and selectivity can be increased by operating at lower temperatures under H<sub>2</sub>, in which case H atoms replace Hg\* as the principal abstracting reagent and H atom abstraction from the  $\alpha$ -CH bond leads directly to the  $\alpha$ -C-centered radical. Under H atom conditions, unsaturated alcohols also react, in which case diols other than the 1,2-isomer can be formed selectively. The product can be rationalized on the basis of H atom addition to the C=C double bond to give the most stable radical which then dimerizes. For the special case of *t*-BuOH, H atom abstraction from the *t*-BuOH  $\beta$ -CH group under H atom conditions leads to the  $\beta$ -C-centered radical, which dimerizes to the 1,4-diol. Radical disproportionation accounts for some of the byproducts observed. The following previously unknown C–H bond strengths (kcal/mol) were determined from the results, assuming the literature BDE for the  $\alpha$ -C–H of 2-propanol (91.0  $\pm$  1.0): *n*-butanol, 92.8  $\pm$  1.0 ( $\alpha$ ), 95.2  $\pm$  1.0 ( $\beta$ ), and 94.3  $\pm$  1.0 ( $\gamma$ ); *n*-propanol, 93.1  $\pm$  1.0 ( $\alpha$ ) and 95.0  $\pm$  1.0 ( $\beta$ ), respectively.

## Introduction

Glycols are usually synthesized from compounds of the same carbon number, for example, by osmylation<sup>1</sup> of an alkene or the hydrolysis of an epoxide.<sup>1</sup> Less common are routes that involve C–C bond formation, such as the pinacol reaction.<sup>2</sup>

Mercury-photosensitized reactions are well-known,<sup>3a–d</sup> but have only rarely been used for synthetic purposes. We have developed an apparatus (Figure 1) in which a variety of organic compounds can be dehydrodimerized on a preparative scale by mercury-photosensitized reaction in the vapor phase. The reactions are carried out in ordinary photochemical equipment, either at the reflux temperature of the substrate under an inert atmosphere<sup>4a–g</sup> or at a somewhat lower temperature under hydrogen.<sup>4h–j</sup> Quantum yields are normally in the range 0.2–0.8. Chemical yields are normally 60–95%. Although the reaction involves radical intermediates, it is not a chain process. Prior work strongly suggests the steps shown below (eqs 1–5), illustrated for the case of an alkane, are responsible for the chemistry observed. A low-pressure Hg lamp selectively excites the vapor phase Hg, but not the Hg dissolved in the liquid phase, to the <sup>3</sup>P<sub>1</sub> state (Hg\*), which

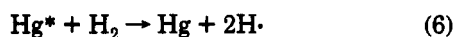
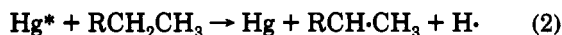


**Figure 1.** The apparatus for preparative-scale mercury-photosensitized dehydrodimerization.

homolyzes a substrate C–H bond (eq 2). The H atoms formed cannot recombine efficiently in the vapor and so they tend to abstract H atoms from the substrate (eq 3). Recombination and disproportionation of the C-centered radicals lead to the product and to alkene (eq 4). The latter rejoins the radical pool after fast H atom attack (eq 5). Since the product is involatile, it collects in the liquid phase where it is protected from further attack.

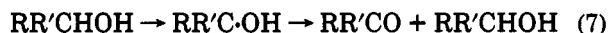
Under an H<sub>2</sub> atmosphere, H<sub>2</sub> is far more reactive than the organic substrate toward Hg\* attack, probably because Hg\*/H<sub>2</sub> collisions are the most frequent<sup>4d</sup> and eq 6

- (1) Gunstone, F. D. *Adv. Org. Chem.* **1960**, 103.  
 (2) Huffman, J. W. *Acc. Chem. Res.* **1983**, 16, 399.  
 (3) (a) Cvetanovic, R. *J. Progr. React. Kinet.* **1964**, 2, 77. (b) Taylor, H. S.; Hill, D. G. *J. Am. Chem. Soc.* **1929**, 51, 2922. (c) Steacie, E. W. R.; Philip, N. W. F. *J. Phys. Chem.* **1938**, 6, 179. (d) Steacie, E. W. R. *Atomic and Free Radical Reactions*; Reinhold: New York, 1954; 2v.  
 (4) (a) Brown, S. H.; Crabtree, R. H. *Tetrahedron Lett.* **1987**, 28, 5599. (b) Brown, S. H.; Crabtree, R. H. *J. Chem. Educ.* **1988**, 65, 290. (c) Brown, S. H.; Crabtree, R. H. U.S. Patent 4,725,342, 1988. (d) Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, 111, 2935, 2946. (e) Muedas, C. A.; Ferguson, R. R.; Crabtree, R. H. *Tetrahedron Lett.* **1989**, 30, 3389. (f) Boojamra, C. G.; Muedas, C. A.; Ferguson, R. R.; Crabtree, R. H. *Tetrahedron Lett.* **1989**, 30, 5583. (g) Ferguson, R. R.; Crabtree, R. H. *Nouv. J. Chem.* **1989**, 13, 647. (h) Ferguson, R. R.; Boojamra, C. G.; Brown, S. H.; Crabtree, R. H. *Heterocycles* **1989**, 28, 121. (i) Muedas, C. A.; Ferguson, R. R.; Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* **1991**, 113, 2233. (j) Ferguson, R. R.; Krajncik, P.; Crabtree, R. H. *Synlett* **1991**, 9, 597.



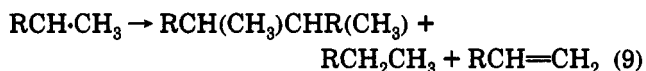
dominates the chemistry. The H atoms formed in this way then attack the substrate by eq 3. A key feature of both the  $\text{Hg}^*$  and H atom systems is that the liquid phase is not reactive,<sup>4d</sup> so that the dehydrodimer is protected from further conversion by condensation. This allows us to obtain high yields at high conversion.

Prior work<sup>3</sup> suggests that alcohols undergo O-H not C-H bond homolysis on reactive collision with  $\text{Hg}^*$ . Only C-C dehydrodimers are seen and so the  $\text{RCH}\cdot\text{OH}$  radical is thought to be formed in a subsequent H abstraction from  $\text{RCH}_2\text{OH}$  by  $\text{RCH}_2\text{O}\cdot$ . A significant side reaction is disproportionation (eq 7) to give aldehyde or ketone.



Fortunately, for lower alcohols these disproportionation products are volatile enough to be swept out the reactor by the gas stream.

Compounds with C=C bonds react under H atom conditions by H atom addition to the C=C bond to give predominantly the more stable of the two possible radicals, which then recombine. If the alkene in question contains OH groups, non- $\alpha,\alpha$ -diols can be formed. The key reactions are shown in eqs 8 and 9.



Our previous work<sup>4a-j</sup> has been directed at discovering the scope of the reaction, but we now report a detailed study of the dimerization of perhaps the most important class of substrates, simple alcohols.

## Results and Discussion

**Selectivity.** To make the alcohol dehydrodimerization reaction useful for preparative purposes, we need to have some idea of the selectivity pattern and how it can be manipulated by changing the conditions. Prior to our own work, only methanol dehydrodimerization to ethylene glycol had been studied.<sup>7a,b</sup> As we have briefly reported,<sup>4d</sup> higher alcohols also react. We now study these reactions in detail under both argon and hydrogen atmospheres.

Ethanol reacts under argon at reflux to give the  $\alpha,\alpha$ -dimer as a 50:50 mixture of the *meso* and *d,l* forms. These

constitute 80.9%<sup>5</sup> of the involatiles remaining after the excess ethanol has been removed by vacuum distillation. Under a hydrogen atmosphere, the corresponding percentage for the  $\alpha,\alpha$ -dimer product is 76.9%. The *meso/d,l* ratio is again very close to unity. None of the  $\alpha,\beta$ - and  $\beta,\beta$ -dimers are present in either case as shown by GC/MS comparison with authentic samples. The high selectivity for the  $\alpha,\alpha$ -dimer is understandable because the C-H bond which is broken is not only  $\alpha$  to oxygen but also secondary. This makes it substantially weaker than the  $\beta$  C-H and therefore especially sensitive to homolysis by  $\text{H}\cdot$  (or  $\text{RO}\cdot$ ). The literature<sup>8</sup>  $\alpha$ -C-H bond strength for EtOH is  $93 \pm 1$  kcal/mol and the  $\beta$ -C-H bond strength may be ca. 100 kcal/mol by analogy with that for Et-H ( $101.2 \pm 0.5$ ). Under hydrogen, the rate is 1.31 times faster (Table I) than under argon. The two-step process with  $\text{Hg}^*/\text{H}_2$  collisions generating H atoms which subsequently abstract from the substrate therefore seems to be more efficient than direct  $\text{Hg}^*/\text{substrate}$  reactions. This is reasonable since the quantum yield for H atom formation in  $\text{Hg}^*/\text{H}_2$  collisions is unity<sup>4j</sup> and H atoms are known to be efficient abstractors from C-H bonds.<sup>4i</sup> The ratio of  $\alpha,\alpha$ -dimer in the involatile fraction, 76.9%, is about the same as  $\text{Hg}^*/\text{Ar}$  case.

The case of 1-propanol allows us to compare the rate of attack at secondary C-H bonds  $\alpha$  and  $\beta$  to oxygen. We find that the  $\alpha,\alpha$ -dimer is still the major product (85.0% for  $\text{Hg}^*/\text{Ar}$  and 77.0% for  $\text{Hg}^*/\text{H}_2$ ) and the *meso/d,l* ratio remains close to unity ( $1.00 \pm 0.05$ ). Although the selectivity for  $\alpha,\alpha$ -dimer for  $\text{Hg}^*/\text{H}_2$  conditions is 8% less than for  $\text{Hg}^*/\text{Ar}$ , the rate of  $\alpha,\alpha$ -dimer production is 1.24 times faster for  $\text{Hg}^*/\text{H}_2$ . The  $\alpha,\beta$ -dimer is present in 13.7% ( $\text{Hg}^*/\text{Ar}$ ) and 14.4% ( $\text{Hg}^*/\text{H}_2$ ) which implies that the  $\beta$  position is about 0.07 times as reactive as the  $\alpha$  position per C-H bond under both reaction conditions. The authentic  $\alpha,\beta$ -dimer can be synthesized by an aldol condensation of propionaldehyde followed by reduction of the product with  $\text{NaBH}_4$ . The result can be confirmed by running an  $\text{Hg}^*/\text{H}_2$  reaction with 1-propanol and allyl alcohol. 1-Propanol gives largely the  $\alpha$ -radical and therefore the  $\alpha,\alpha$ -dimer when run on its own. Allyl alcohol gives largely the  $\beta$ -radical, by terminal H atom addition, to give the more stable secondary radical, and therefore the  $\beta,\beta$ -dimer when run on its own. A mixture of the two alcohols gives the  $\alpha,\alpha$ ,  $\alpha,\beta$  and  $\beta,\beta$ -dimers by statistical recombination of both types of radical. From these types of experiments, a wide variety of dimers can be identified in this and related reactions.

2-Propanol dimerizes to give pinacol as the only dimer under either  $\text{Hg}^*/\text{Ar}$  or  $\text{Hg}^*/\text{H}_2$  conditions. In this case, we also looked for the disproportionation product, acetone, by passing the exit gases through a cold trap ( $-78^\circ\text{C}$ ). In this case, 10 g of 2-propanol under  $\text{H}_2$  gave 1.20 g of pinacol after 24 h, while 3.70 g of acetone were collected in the cold trap and 4.87 g of 2-propanol were recovered from the trap and the reactor, giving an exceptionally good mass

(5) This percentage refers to the mole fraction of  $\alpha,\alpha$ -dimer in the final product mixture of involatile materials after the photochemical step. This number is not a yield, because excess alcohol is always used, some of which is entrained by the gas stream and lost from the apparatus; some of the aldehyde disproportionation products are also lost in this way. These percentage values and the weights of involatile fraction formed per hour were repeatable, while numbers for yields were not, because of differential losses of starting materials in different experiments.

(6) Cier, H. E. U.S. Patent 2,640,023, May 26, 1953.

(7) Wijnen, M. H. *J. Chem. Phys.* 1957, 27, 710. *Ibid.* 1958, 28, 271. Porter, R. P.; Noyes, W. A. *J. Am. Chem. Soc.* 1959, 81, 2307.

(8) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* 1982, 33, 493.

Table I. Selected Substrates and Products from Some Dehydrodimerizations of Alcohols

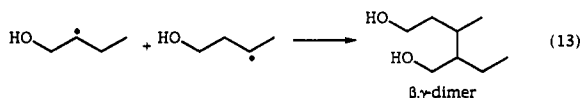
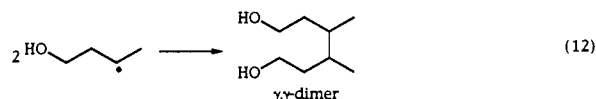
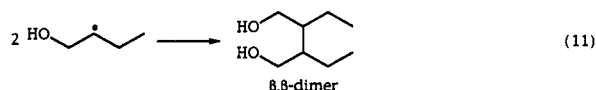
method	substrate	major product	rate <sup>a</sup> of dimer formation (mmol/h)	% <sup>b</sup>	<i>d,l/meso</i>	$\alpha,\beta$ (%)	$\alpha,\gamma$ (%)
Hg*/Ar	EtOH	2,3-butanediol	0.86	80.9	~1	0	—
Hg*/H <sub>2</sub>	EtOH	2,3-butanediol	1.13	76.9	~1	0	—
Hg*/Ar	1-PrOH	3,4-hexanediol	0.78	85.0	~1	11.7	—
Hg*/H <sub>2</sub>	1-PrOH	3,4-hexanediol	0.97	77.0	~1	11.1	—
Hg*/Ar	2-PrOH	pinacol	0.27	100	—	—	—
Hg*/H <sub>2</sub>	2-PrOH	pinacol	0.47	100	—	—	—
Hg*/Ar	1-BuOH	4,5-octanediol	0.32	40.6	~1	4.60	11.1
Hg*/H <sub>2</sub>	1-BuOH	4,5-octanediol	0.67	61.5	~1	7.50	21.8
Hg*/Ar	<i>t</i> -BuOH	2,5-dimethyl-2,5-hexanediol	0.02	100	—	—	—
Hg*/H <sub>2</sub>	<i>t</i> -BuOH	2,5-dimethyl-2,5-hexanediol	0.14	100	—	—	—
Hg*/Ar	NpOH	2,2,5,5-tetramethyl-3,4-hexanediol	0.70	86.3	1.76	—	—
H*/H <sub>2</sub>	NpOH	2,2,5,5-tetramethyl-3,4-hexanediol	1.14	76.8	1.76	—	—

<sup>a</sup> Rate of dimer formation is calculated from reactions using a 220-cm<sup>3</sup> reactor. <sup>b</sup> Percentage of major product in involatile fraction.

balance of 97%. Again, the rate of dimer production under H<sub>2</sub> is 1.74 times faster than under Ar.

1-Butanol also gives the  $\alpha,\alpha$ -dimer, but this compound only constitutes 40.6% (Hg\*/Ar) and 61.5% (Hg\*/H<sub>2</sub>) of the involatile dimer fractions. The relatively low yield of the  $\alpha,\alpha$ -dimer suggested that a significant fraction of the remaining dimers might have been formed by C-H bond breaking at non- $\alpha$  positions or from the disproportionation products undergoing subsequent reaction with the alcohols and so complicating the product mixture. Since the  $\alpha,\alpha$ -dimer is still the major product from *n*-BuOH,  $\alpha$ -radicals must still predominate in the vapor and so the non- $\alpha$  radicals (call then  $\xi$ -radicals) are likely to end up in  $\alpha,\xi$ -dimers. Given that primary C-H bonds are unlikely to react, the logical non- $\alpha,\alpha$ -dimers to look for are  $\alpha,\beta$  and  $\alpha,\gamma$ . The authentic  $\alpha,\beta$ -dimer can be easily made by the aldol condensation of butyraldehyde followed by NaBH<sub>4</sub> reduction. This allows the  $\alpha,\beta$ -dimer to be identified in the dimer mixture. The ratio of  $\alpha,\beta$ - to  $\alpha,\alpha$ -product proves to be 4.60 (Hg\*/Ar) and 7.50% (Hg\*/H<sub>2</sub>). The  $\alpha,\gamma$ -dimer identified as discussed below constitutes a substantial 11.1 (Hg\*/Ar) and 21.8% (Hg\*/H<sub>2</sub>) of the involatile fraction.

We have discussed how the  $\alpha,\alpha$  and  $\alpha,\beta$ -dimers were identified. The other dimers were made by H atom addition to the appropriate unsaturated precursors.<sup>41</sup> For example, eqs 10-13 show how a mixture of the  $\beta,\beta$ -,  $\beta,\gamma$ -



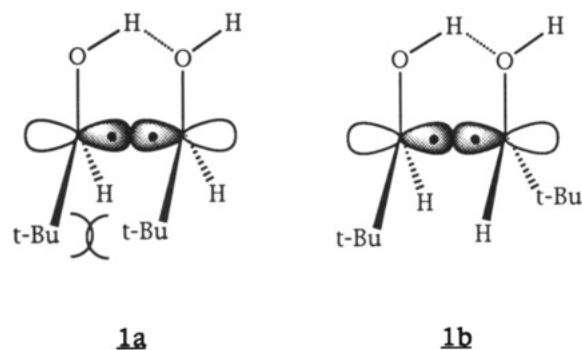
and  $\gamma,\gamma$ -dimers was prepared by hydrodimerizing but-2-ene-1-ol which gives approximately equal amounts of  $\beta$  and  $\gamma$  radicals on H addition. Comparison of the GC/MS and <sup>13</sup>C NMR data for the  $\beta,\beta$ -,  $\beta,\gamma$ -, and  $\gamma,\gamma$ -dimers from but-2-ene-1-ol and for the  $\gamma,\gamma$ -dimer from but-3-ene-1-ol allowed identification of all these isomers. None of these dimers was present in the 1-butanol dehydrodimerization product mixture in significant amount, however. This left the  $\alpha,\gamma$ -dimer as the most reasonable possibility for

the unidentified minor dehydrodimer from 1-butanol. This we made by running an Hg/H<sub>2</sub> reaction with 1-butanol and but-2-ene-1-ol, in which case we were able to detect all the expected homo- and cross-dimers from a mixture of  $\alpha$ ,  $\beta$ , and  $\gamma$  radicals and eliminate the dimers previously identified and so identify the  $\alpha,\gamma$ -dimer.

Previous studies<sup>41</sup> have shown that the radicals recombine statistically, so that the expected  $\alpha,\alpha/\alpha,\beta/\alpha,\gamma$  dimer ratio should be  $(R_\alpha)^2:2(R_\alpha)(R_\beta):2(R_\alpha)(R_\gamma)$ , where  $R_\xi$  is the fraction of radicals at any position  $\xi$ ;  $R$  is therefore a measure of reactivity at that site. Having the composition of the dimer fraction from 1-BuOH in hand, we were able to deduce  $R_\alpha:R_\beta:R_\gamma$ , the ratio of radicals that would give rise to this product mixture by statistical recombination, which is 100:5.70:13.7 (Hg\*/Ar) and 100:6.10:17.8 (Hg\*/H<sub>2</sub>). These are the relative rates of attack at  $\alpha$ ,  $\beta$ , and  $\gamma$  sites for Hg\*/Ar and Hg\*/H<sub>2</sub> conditions. We see an interesting alternation of reactivity. The  $\alpha$  position is most activated by being next to the heteroatom. The  $\beta$  position is the least reactive, presumably because it is deactivated by the inductive effect of the oxygen without benefiting from electron donation from the oxygen lone pairs. The  $\gamma$  position is further removed from oxygen and so the deactivating effect of the inductive effect is diluted. This strongly suggests that if we extended this chemistry to longer straight-chain alcohols, the  $\delta,\epsilon,\dots$  groups would have a similar reactivity to the  $\gamma$  CH<sub>2</sub> of 1-butanol and therefore be sufficiently reactive to cause a severe decrease in selectivity for  $\alpha,\alpha$ -dimers.

In order to look at C-H bond breaking at a site remote from the oxygen atom, we choose *t*-BuOH, which does not contain any  $\alpha$  C-H bonds but has nine primary  $\beta$ -C-H bonds. Under Hg\*/Ar conditions, the rate of dimer production is certainly slower than for alcohols contain  $\alpha$  C-H bond, but the reaction takes place cleanly and produces 2,5-dimethyl-2,5-hexanediol which constitutes nearly 100% of the involatile fraction. The rate of dimer production is 7 times faster under H<sub>2</sub> than under Ar and becomes comparable in efficiency with the dimerization of *n*-BuOH. This product was recrystallized from *n*-hexane and unambiguously characterized by MS, mp, and <sup>13</sup>C NMR.

Neopentyl alcohol dimerized smoothly at reflux to give  $\alpha,\alpha$ -dimer under both reaction conditions (86.3% for Hg\*/Ar and 76.8% for Hg\*/H<sub>2</sub>). For the first time the *d,l/meso* ratio is no longer 1:1 but 64:36, no doubt reflecting the bulk of the *t*-Bu groups. The hydrogen-bonded transition states 1a and 1b (Figure 2) rationalize the predominance of the *d,l* compound derived from 1b. The *meso*-isomer of the resulting 2,2,5,5-tetramethyl-3,4-hexanediol reacts much faster with 2,2-methoxypropane than



**Figure 2.** The hydrogen-bonded transition states **1a** and **1b** rationalize the predominance of the *d,l* compound derived from **1b**.

does the *d,l*-form, which allows each dimer to be separated and individually characterized by  $^{13}\text{C}$  NMR,  $^1\text{H}$  NMR, mp, and MS. This is an inexpensive route to these compounds, which are relatively difficult to make.

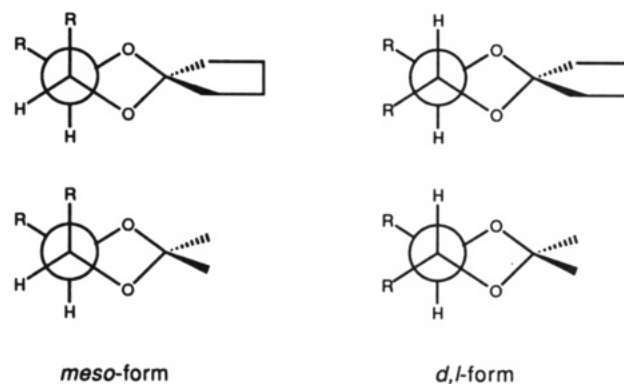
**Bond Strength Estimates.** Earlier work<sup>4d,i</sup> showed that the relative rates of C–H bond cleavage for different C–H bonds depends on the bond strength difference as given by Cier's equation<sup>6</sup> (eq 14), in which  $r_1/r_2 =$

$$r_1/r_2 = (b_2/b_1) \{ \exp\{(E_1 - E_2)/2RT\} \} \quad (14)$$

$\{N_1(c)\}^{1/2}/\{N_2(a)\}^{1/2}$ ,  $N_n$  is the mole fraction of  $R_n - \text{H}$  in the vapor-phase mixture,  $a$  and  $c$  are the molar percentages of  $R_1$  and  $R_2$  in the dimeric products at short reaction time,  $b$  is the number of C–H bonds (counting only the weakest type), and  $E$  is the bond strength of the weakest C–H bonds. Related treatments exist.<sup>13a-d</sup> Equation 14 is derived<sup>13e</sup> from the Arrhenius equation, which relates the rate constants to the activation energy, and the Evans–Polanyi relationship, which relates the activation energy to the bond strength in a series of similar reactions.

From the observed  $R_1 - R_1 : R_1 - R_2 : R_2 - R_2$  product ratios at short reaction time in an experiment employing a mixture of  $R_1 - \text{H}$  and  $R_2 - \text{H}$ , we can estimate the relative bond strengths involved. The numbers obtained from  $\text{Hg}^*/\text{Ar}$  and  $\text{Hg}^*/\text{H}_2$  differ little, but we prefer those from  $\text{Hg}^*/\text{H}_2$  because there is a risk that the  $\text{Hg}^*/\text{Ar}$  numbers might be affected by  $\text{Hg}^*$ -alcohol exciplex formation.

In order to estimate the bond strength of different C–H bonds in *n*-butanol, we chose to cross-dimerize it with 2-propanol which has a known  $\alpha$ -C–H bond strength<sup>8</sup> of  $91.0 \pm 1.0$  kcal/mol and only gives  $\alpha$ -radicals. We ran an  $\text{Hg}^*/\text{H}_2$  experiment with 32.8 mmol of *n*-butanol and 48.2 mmol of 2-propanol at reflux. After 2 h, the product mixtures contain very largely pinacol and 2-methyl-2,3-hexanediol in a 69.9:30.1 mole ratio. This allows us to estimate an  $\alpha$ -C–H bond strength of  $92.8 \pm 1.0$  kcal/mol for *n*-butanol. Having established this value, we can now



**Figure 3.** The NMR signals of diastereotopic alkyl groups on C-2 are used to identify the *meso*- and *d,l*-glycols.

use the relative reactivity of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -sites in 1-BuOH to estimate the  $\beta$ - and  $\gamma$ -C–H bond strengths of  $95.2 \pm 1.0$  and  $94.3 \pm 1.0$  kcal/mol, respectively. By the same strategy, 81.4% of pinacol and 18.6% of 2-methyl-2,3-pentanediol were identified in the cross-dimerization of 2-propanol with *n*-propanol. This leads to C–H bond strengths of  $93.1 \pm 1.0$  kcal/mol ( $\alpha$ ) and  $95.0 \pm 1.0$  kcal/mol ( $\beta$ ) for *n*-propanol. None of these bond strengths have been previously determined. Relative to 2-propanol, the error in the BDE is probably no more than  $\pm 1.0$  kcal/mol, as is substantiated by the similarity of the product ratios whether  $\text{Hg}^*$  or  $\text{H} \cdot$  is the abstractor.

**Identifying the *meso*- and *d,l*-Diastereomers.** We have developed a simple way to distinguish the *meso*- from the *d,l*-dimers in an unambiguous way, which relies on the presence or absence of diastereotopic signals in the  $^{13}\text{C}$  NMR of the cyclopentanone ketals. These were formed from the glycol and cyclopentanone with *p*-toluenesulfonic acid catalyst at reflux in benzene for 5 h. The products were fully characterized as the expected ketals. As shown in Figure 3, only the *meso*-ketal leads to diastereotopy in the ring carbons of the cyclopentane ring. For the ketal from *meso*-4,5-octanediol, these pairs resonate at  $\delta$  23.26, 23.64 and  $\delta$  37.17, 37.88. Interestingly, the corresponding resonances of the *d,l*-form are not only single, as expected from symmetry considerations, but they appear at  $\delta$  23.26 and 37.46, almost exactly halfway between the resonances of the *meso*-form. Although the neopentanol dimers fail to form a ketal with cyclopentanone, the less bulky 2,2-dimethoxypropane can be used instead. In this case, the  $\text{CH}_2$  protons are again well-separated at  $\delta$  1.32 and 1.48. The *d,l*-form shows a single peak at  $\delta$  1.38. The *meso/d,l* ratios can be estimated by NMR integration of the mixture of ketals.

**Disproportionation Products.** We expected to observe disproportionation products in these reactions along with the dimer. For example, the radicals from ethanol should not only give the glycol, but also ethanol and acetaldehyde. The ethanol formed is indistinguishable from the starting material, but the acetaldehyde might be expected to accumulate in the products, perhaps undergo photochemistry, and complicate the product mixture. An advantage of the reflux method is that acetaldehyde has a much lower bp than the alcohol and so tends to be entrained in the hydrogen stream leaving the apparatus. As we have seen in the case of 2-propanol, acetone was detected by condensing the exit vapors.

As the molecular weight of the starting alcohol rises, the volatility of the aldehyde decreases and more of it

(9) Adams, R.; Adams, E. W. *Organic Syntheses*; Wiley: New York, 1941, Collect. Vol. I, p 459.

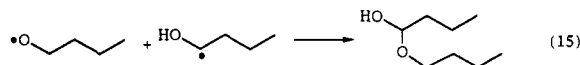
(10) Favorskaya, T. A.; Ryzhova, N. P. *J. Gen. Chem. USSR* 1956, 26, 447.

(11) Cadwallader, E. A.; Fookson, A.; Mears, T. W.; Howard, F. L. *J. Res. Natl. Bur. Stand.* 1948, 41, 111.

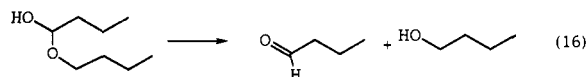
(12) Young, W. G.; Levanas, L.; Jasaitis, Z. *J. Am. Chem. Soc.* 1936, 58, 2274.

(13) (a) Gunning, H. E.; Campbell, J. M.; Sandhu, H. S.; Strausz, O. P. *J. Am. Chem. Soc.* 1973, 95, 746–751. (b) *Handbook of Chemistry and Physics*, 68th ed.; CRC Press: Boca Raton, FL, 1987–1988. (c) Kerr, J. A. *Chem. Rev.* 1966, 66, 465. (d) Golden, D. M.; Benson, S. W. *Chem. Rev.* 1969, 69, 125. (e) Brown, S. Ph.D. Thesis, Yale University, 1988, Chapter 5.

therefore remains in the apparatus. In the case of neopentanol, where the aldehyde tends not to escape because it is not sufficiently volatile, the  $\text{Me}_3\text{CCHO}$  is detected in the form of its derivative pivalon  $(\text{CH}_3)_3\text{CC}(\text{=O})\text{CH}(\text{OH})\text{C}(\text{CH}_3)_3$  which constitutes 6% of the involatile dimer fraction. In the case of 1-butanol ( $\text{Hg}^*/\text{Ar}$ ), the major side product is again a derivative of the aldehyde disproportionation product, this time butanal dibutyl acetal  $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{O}-n\text{Bu})_2)$ . Its identity was confirmed by comparison with an authentic sample synthesized from *n*-butanol and butyraldehyde with catalytic amount of TFA. Since formation of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{O}-n\text{Bu})_2$  from the aldehyde and the alcohol is very slow in the absence of acid, we think the formation of the acetal from 1-BuOH ( $\text{Hg}^*/\text{Ar}$ ) may also be formed from the recombination of *n*-BuO $\cdot$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}\text{-OH}$  to give the hemiacetal. Once formed via eq 15, the hemiacetal



can react with butyraldehyde, lose water to give the observed  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{O}-n\text{Bu})_2$ , or cleave to give *n*-butanol and butyraldehyde (eq 16).



### Conclusions

Simple alcohols can be dehydrodimerized to diols by Hg photosensitization. Similar selectivity was observed under argon and hydrogen atmospheres, but  $\text{H}_2$  slightly favored the 1,2-diol. C-H bond strengths were estimated for the  $\text{CH}_2$  groups of *n*-butanol and *n*-propanol.  $\text{Hg}^*/\text{H}_2$  conditions give H atoms, which can be used in the dehydrodimerization of saturated substrates, in which case the weakest C-H bonds are attacked. Alternatively, H-atom addition to unsaturated substrates leads to non- $\alpha,\alpha$ -dimers, either as single isomers or simple mixtures.

### Experimental Section

NMR spectra were determined on a GE QE-plus 300-MHz or Bruker 250-MHz instrument, and GC/MS analysis was carried out on a HP 5890 Gas Chromatograph (29 m, 0.25 mm i.d. capillary column coated with a 0.25  $\mu\text{m}$  film of SE 30) connected with a HP 5972A MS-detector. Substrates were used as received from Aldrich Chemical Co., Fluka Corp., or Kodak Corp. **Caution:** Mercury vapor is toxic and appropriate precautions must be taken, but no organomercury compounds have been detected in these systems. We assume that GC response factors are the same for isomers having the same carbon numbers.

**General Method I** ( $\text{Hg}^*/\text{Ar}$  conditions). Dimerizations were carried out following the method of Brown and Crabtree.<sup>4d</sup>

**General Method II** (saturated alcohols under  $\text{Hg}^*/\text{H}_2$  conditions). Dimerizations were carried out following the method of Muedas, Ferguson, Brown, and Crabtree.<sup>4b</sup>

**General Method III** (unsaturated alcohols under  $\text{Hg}^*/\text{H}_2$  conditions). The method described by Muedas, Ferguson, and Crabtree<sup>4c</sup> was employed.

**Details for Individual Compounds.** The data are normally reported as follows: product, method used, percentage in involatile fraction, isolation,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS, and mp.

**2,3-Butanediol.** Method I or II; constitutes 80.9% (method I), 76.9% (method II) of involatile fraction. Isolated by flash column chromatography (75% *n*-hexane, 25% ethyl acetate):  $^{13}\text{C}$  NMR  $\delta$  74.21, 70.72 (tertiary CH), 18.92, 16.61 (Me); MS (70 eV) 90 ( $\text{M}^+$ ), 57 ( $\text{M}^+ - \text{H}_2\text{O} - \text{CH}_3$ ), 45 ( $\text{M}^+ - \text{HC}(\text{OH})(\text{CH}_3)$ , base peak).

**3,4-Hexanediol.** Method I or II; 85.0% (method I), 77.0% (method II). Isolated by flash column chromatography (80% *n*-hexane, 20% ethyl acetate):  $^{13}\text{C}$  NMR  $\delta$  75.83, 75.10 (tertiary CH), 26.01, 23.90 (secondary  $\text{CH}_2$ ), 10.21, 9.75 (Me); MS (70 eV) 89 ( $\text{M}^+ - \text{C}_2\text{H}_5$ ), 59 ( $\text{M}^+ - \text{HC}(\text{OH})(\text{CH}_2\text{CH}_3)$ , base peak).

**2,4-Dimethyl-2,4-butanediol (Pinacol).** Method I or II; 99% (method I), 99% (method II). Isolated by flash column chromatography (75% *n*-hexane, 25% ethyl acetate):  $^1\text{H}$  NMR  $\delta$  1.17 (s, 12H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR  $\delta$  24.8 ( $\text{CH}_3$ ), 75.0 (COH); MS (70 eV) 103 ( $\text{M}^+ - \text{CH}_3$ ), 85 ( $\text{M}^+ - \text{H}_2\text{O} - \text{CH}_3$ ), 59 (base peak); obsd mp 39–40.5  $^\circ\text{C}$ , lit.<sup>9</sup> mp 40–43  $^\circ\text{C}$ .

**4,5-Octanediol.** Method I or II; 40.6% (method I), 61.5% (method II). Product was directly crystallized from the reaction mixture and was washed with cold *n*-hexane:  $^{13}\text{C}$  NMR  $\delta$  74.30, 73.98 (tertiary CH), 35.52, 33.27, 18.71, 18.63 (secondary  $\text{CH}_2$ ), 13.87 (Me); MS (70 eV) 103 ( $\text{M}^+ - \text{C}_3\text{H}_7$ ), 73 ( $\text{M}^+ - \text{HC}(\text{OH})\text{Pr}$ ), 55 (base peak); obsd mp 121.5–122  $^\circ\text{C}$ , lit.<sup>12</sup> mp 123.5–124.5  $^\circ\text{C}$ .

**2-Ethyl-1,3-hexanediol.** Method I or II; 4.60% (method I), 7.50% (method II); the colorless and slightly oily liquid was isolated by flash column chromatography (75% *n*-hexane, 25% ethyl acetate):  $^1\text{H}$  NMR  $\delta$  0.89 (t, 6H,  $\text{CH}_3$ ), 1.25–1.52 (m, 8H,  $\text{CH}_2$ , CH), 3.60–3.84 (m, 3H,  $\text{CH}_2\text{OH}$  and  $\text{CHOH}$ );  $^{13}\text{C}$  NMR  $\delta$  11.49, 12.06, 13.87 ( $\text{CH}_3$ ), 17.86, 18.68, 19.27, 21.19, 34.98, 37.52 ( $\text{CH}_2$ ), 63.38, 63.94, ( $\text{CH}_2\text{OH}$ ), 45.52, 45.74 (CH), 74.57, 74.92 (CHOH); MS (70 eV) 103, 73, 56 (base peak).

**3-Methyl-1,4-heptanediol.** Method I or II; 11.1% (method I), 21.8% (method II). Isolated by flash column chromatography (60% *n*-hexane, 40% ethyl acetate) as a colorless liquid:  $^1\text{H}$  NMR  $\delta$  0.83–0.89 (m, 6H,  $\text{CH}_3$ ), 1.26–1.70 (m, 5H,  $\text{CH}_2$ , CH), 3.51–3.70 (m, 3H,  $\text{CHOH}$ ,  $\text{CH}_2\text{OH}$ );  $^{13}\text{C}$  NMR  $\delta$  13.70, 13.93, 16.31 ( $\text{CH}_3$ ), 18.79, 19.40, 35.01, 35.41, 35.81, 36.37 ( $\text{CH}_2$ ), 35.81, 36.21 (CH), 59.95, 60.24 ( $\text{CH}_2\text{OH}$ ), 74.38, 75.25 (CHOH); MS (70 eV) 103, 85 (base peak), 56.

**2,2,5,5-Tetramethyl-3,4-hexanediol.** Method I or II; 86.3% (method I), 76.8% (method II). The product was directly crystallized from the reaction mixture and was washed with *n*-hexane; isomer separation and spectral data follow.

***d,l*-2,2,5,5-Tetramethyl-3,4-hexanediol.** To a 2,2-dimethoxypropane solution (4 mL) of 2,2,5,5-tetramethyl-3,4-hexanediol (130 mg, 0.74 mmol) formed as above was added a catalytic amount of  $\text{CF}_3\text{COOH}$ . The reaction was refluxed for 2.5 h and the unreacted *d,l*-diol was isolated by flash chromatography (88% *n*-hexane, 12% ethyl acetate) as colorless crystals melting at 123–124  $^\circ\text{C}$ :  $^1\text{H}$  NMR  $\delta$  3.32 (d, 2H,  $J = 5.5$  Hz, tertiary CH), 2.26 (d, OH,  $J = 5.5$  Hz), 0.90 (s, 18H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR  $\delta$  74.97 (COH), 35.19 (quaternary C), 25.81 (Me); MS (70 eV) 117 ( $\text{M}^+ - \text{C}(\text{CH}_3)_3$ ), 87 ( $\text{M}^+ - \text{HC}(\text{OH})(\text{C}(\text{CH}_3)_3)$ , base peak).

***meso*-2,2,5,5-Tetramethyl-3,4-hexanediol.** To a solution of 30 mg (0.12 mmol) of 2,2-dimethyl-*cis*-4,5-di-*tert*-butyl-1,3-dioxolane in 1 mL of ethyl acetate at 25  $^\circ\text{C}$  was added a catalytic amount  $\text{CF}_3\text{COOH}$ . After stirring overnight, the product was purified by sublimation at 100  $^\circ\text{C}$  as colorless crystals melting at 118–120  $^\circ\text{C}$ :  $^1\text{H}$  NMR  $\delta$  3.24 (br, 2H, tertiary CH), 1.48 (br, OH), 1.00 (s, 18H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR  $\delta$  80.41 (COH), 35.63 (quaternary C), 26.54 (Me); MS (70 eV) 117 ( $\text{M}^+ - \text{C}(\text{CH}_3)_3$ ), 87 ( $\text{M}^+ - \text{HC}(\text{OH})(\text{C}(\text{CH}_3)_3)$ , base peak).

**2,2-Dimethyl-*cis*-4,5-di-*tert*-butyl-1,3-dioxolane.** To a solution of racemic 2,2,5,5-tetramethyl-3,4-hexanediol (130 mg, 0.74 mmol) in 4 mL of 2,2-dimethoxypropane was added a cat. amount of  $\text{CF}_3\text{COOH}$ . The mixture was refluxed for 2.5 h and product isolated by flash chromatography (88% *n*-hexane/12% ethyl acetate):  $^{13}\text{C}$  NMR  $\delta$  102.10 (C-2), 86.26 (C-4, C-5), 29.16 (c), 27.25, 27.00 (*Me-C*), 22.63, 14.08 (Me);  $^1\text{H}$  NMR  $\delta$  3.74 (s, 2H, tertiary CH), 1.48 (s, 3H,  $\text{O}_2(\text{CH}_3)\text{CCH}_3$ ), 1.32 (s, 3H,  $\text{O}_2(\text{CH}_3)\text{-CCH}_3$ ), 1.05 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ); MS (70 eV) 199 ( $\text{M}^+ - \text{CH}_3$ ), 157 ( $\text{M}^+ - \text{C}(\text{CH}_3)_3$ , base peak).

**2,2-Dimethyl-*trans*-4,5-di-*tert*-butyl-1,3-dioxolane.** To a solution of 2,2,5,5-tetramethyl-3,4-hexanediol (130 mg, 0.74 mmol) in 4 mL of 2,2-dimethoxypropane was added a cat. amount of  $\text{CF}_3\text{COOH}$ . The reaction was refluxed for overnight and product was isolated by flash chromatography (88% *n*-hexane/12% ethyl acetate):  $^{13}\text{C}$  NMR  $\delta$  104.8 (C-2), 87.35 (C-4, C-5), 33.60 (C), 28.28 (*Me-C*), 25.13 (Me);  $^1\text{H}$  NMR  $\delta$  3.70 (s, 2H, tertiary CH), 1.38 (s, 6H,  $\text{O}_2(\text{CH}_3)\text{CCH}_3$ ), 0.92 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ); MS (70 eV) 199 ( $\text{M}^+ - \text{CH}_3$ ), 157 ( $\text{M}^+ - \text{C}(\text{CH}_3)_3$ , base peak).

**3-Hydroxy-2,2,5,5-Tetramethylhexan-4-one (Pivaloin).**

This byproduct of the neopentyl alcohol dimerization (by method I or II) was isolated by flash chromatography (eluted with 88% *n*-hexane/12% ethyl acetate) as colorless crystals melting at 74–75.5 °C, lit.<sup>11</sup> mp 78–79 °C: <sup>1</sup>H NMR δ 4.18 (d, 1H, *J* = 10.9 Hz, tertiary CH), 2.90 (d, OH, *J* = 10.9 Hz), 0.92 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.85 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); MS (70 eV) 116 (M<sup>+</sup> - C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)), 87 (M<sup>+</sup> - HC(=O)(C(CH<sub>3</sub>)<sub>3</sub>), base peak).

**2,5-Dimethyl-2,5-hexanediol.** Method I or II; 99% (method I), 99% (method II). The product was directly crystallized from the reaction mixture and was washed with *n*-hexane: <sup>1</sup>H NMR 1.56 (s, 4H, secondary CH<sub>2</sub>), 1.21 (s, 12H, Me); <sup>13</sup>C NMR δ 29.45

(secondary C), 38.04 (Me), 70.62 (quaternary COH); MS (70 eV) 113 (M<sup>+</sup> - H<sub>2</sub>O - CH<sub>3</sub>), 95 (M<sup>+</sup> - 2H<sub>2</sub>O - CH<sub>3</sub>), 59 (base peak); obsd mp 83–84 °C, lit.<sup>10</sup> mp 88.5–89 °C.

**Acknowledgment.** We thank the Department of Energy and Amoco Corp. for funding.

**Supplementary Material Available:** Derivation for eq 14 (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.