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Synthesis and Reactions of 3-Diazo-1,4-diphenyl-4-hydroxy-2-butanone

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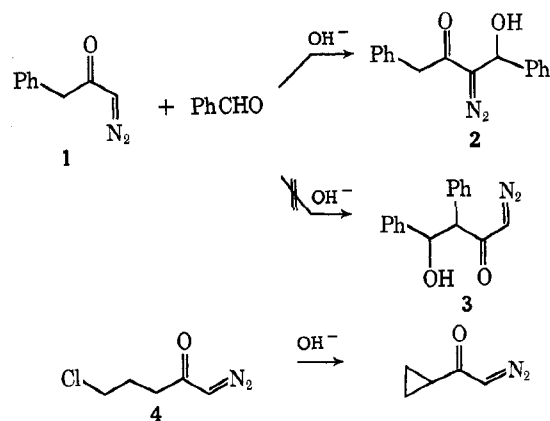
1-Diazo-3-phenyl-2-propanone (**1**) underwent aldol condensation with benzaldehyde at the diazo carbon to give 3-diazo-1,4-diphenyl-4-hydroxy-2-butanone (**2**) in 63% yield. Irradiation of **2** in benzene or methanol below 50° gave 1,4-diphenyl-1,3-butanedione (**5**) in 50% yield. Pyrolysis of **2** in refluxing chlorobenzene gave 40% of **5**. Treatment of **2** with hydrogen chloride in ether gave 20% of the dione **5** and 31% of 3-chloro-1,4-diphenyl-4-hydroxy-2-butanone (**6**). Similarly, when treated with hydrogen bromide in ether, **2** gave 10% of the dione **5** and 45% of 3-bromo-1,4-diphenyl-4-hydroxy-2-butanone (**10**). The structures of **5** and **10** rest on the physical data and their reduction to 2-chloro-1,4-diphenyl-1,3-butanediol (**8**) and 2-bromo-1,4-diphenyl-1,3-butanediol (**11**), respectively.

Under appropriate conditions diazomethyl ketones undergo normal base-catalyzed reactions without the destruction of the $-\text{COCN}_2$ moiety.^{1,2} For example, base-catalyzed intramolecular aldol and Dieckmann-type condensation reactions have been shown to take place at the diazo carbon of some diazomethyl ketones.¹ Normal base-catalyzed intramolecular alkylation can also apparently occur at the α -methylene carbon of a suitable diazomethyl ketone.² Similar intermolecular condensation reactions of diazomethyl ketones, however, have not been investigated.

We wish to report here the first example of a normal base-catalyzed intermolecular condensation reaction of a diazomethyl ketone of the type $\text{RCH}_2\text{COCHN}_2$, which has two potential condensation sites. Successful condensation of 1-diazo-3-phenyl-2-propanone (**1**) with benzaldehyde resulted in exclusive reaction at the diazo carbon to give 3-diazo-1,4-diphenyl-4-hydroxy-2-butanone (**2**). The photochemical, thermal, and acid-catalyzed decompositions of this novel α -diazo- β -hydroxy ketone **2** were also investigated.

Synthesis of 2.—Treatment of a dilute, ethanolic solution of the diazo ketone **1** and an excess of benzaldehyde with 2% sodium hydroxide solution at room temperature resulted in an immediate development of a red color characteristic of diazo ketone decomposition.³ When the solution was held at -5 to 0° and then treated with base, no such color developed but the aldol reaction product was formed. Extraction of the reaction solution with carbon tetrachloride and chromatography of the concentrated extract on alumina gave, besides unreacted starting materials, a deep yellow oil which crystallized to give 3-diazo-1,4-diphenyl-4-hydroxy-2-butanone (**2**) in 63% yield. The infrared spectrum of **2** showed bands at 4.78 and 6.08 μ , confirming retention of the diazo ketone moiety, and a band at 2.94 μ supported the presence of a hydroxyl group. The nmr spectrum of a pure and dry sample of **2** in carbon tetrachloride revealed a doublet at δ 7.21 and a singlet at δ 3.68 due to ten phenyl and two methylene protons, respectively. The one-proton doublets at δ 5.91 ($J = 4$ Hz), and 4.3 ($J = 4$ Hz) were attributed to the methine and the hydroxyl protons,

respectively. Exchange of the hydroxyl proton with deuterium oxide, as judged by the disappearance of the δ 4.3 peak and the collapse of the δ 5.91 peak to a singlet, confirmed this assignment. No evidence for the formation of the aldol product **3** which would have resulted from condensation at the α -methylene carbon was obtained by nmr spectroscopic examination of various chromatographic fractions. The remainder of the unrecovered starting material apparently decomposed during the reaction or the work-up. We cannot, however, eliminate the possible formation of a small amount of **3**.



The fact that **1** condenses with benzaldehyde largely at the diazo carbon contrasts with the intramolecular cyclization of 5-chloro-1-diazo-2-pentanone (**4**) to give cyclopropyldiazomethyl ketone.² The azomethine protons of both **1** and **4** were shown to be more acidic than the respective methylene protons by the addition of a drop of deuterium oxide containing a catalytic amount of sodium carbonate to a carbon tetrachloride solution of **1** or **4**. In both cases the azomethine peak was rapidly and completely removed from the nmr spectra. The methylene peaks in both cases remained unaffected. The cyclization of **4** to give cyclopropyldiazomethyl ketone demonstrates the ease of formation of a three-membered ring over a five-membered ring, probably due to a more favorable entropy of activation for the former process.⁴ The intramolecular alkylation in

(1) T. L. Burkoth, *Tetrahedron Lett.*, 5049 (1969).

(2) N. F. Woolsey and D. D. Hammargren, *ibid.*, 2087 (1970).

(3) P. Yates and D. G. Farnum, *J. Amer. Chem. Soc.*, **85**, 2967 (1963).

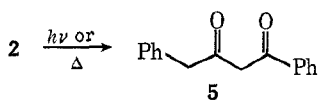
(4) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 198.

addition is irreversible and thus probably rate controlled. Formation of **2** takes place under reversible conditions and probably reflects thermodynamic control of the condensation.

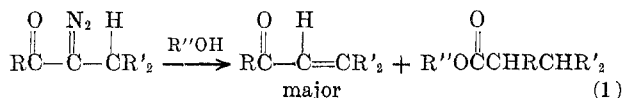
Reactions.—Until recently no α -diazo- β -hydroxy ketones were known.⁵ We were interested in determining to what extent the adjacent hydroxyl group alters or becomes involved in the reactions of the diazo group. To this end three types of reactions of hydroxy-diazo ketone **2** were investigated: pyrolysis, photolysis, and reactions with hydrogen halides.

Pyrolysis.—Pyrolysis of **2** in refluxing chlorobenzene and subsequent evaporation of the solvent gave a yellow oil from which 1,4-diphenyl-1,3-butanedione (**5**) was isolated, *via* its copper salt, in a 40% yield. The remaining material was an intractable oil from which no further pure material could be obtained.

Photolysis.—Photolysis of **2** in benzene or methanolic solution gave dione **5** in 49 and 52% yields, respectively. Thin layer chromatography of the crude photoproduct in each case also revealed the presence of another minor product. A number of efforts, using various separation techniques, were made to obtain this portion of the photoproduct but all of them proved unrewarding. The yields of the dione **5** are considered minimal because its recovery from the reaction mixture proved difficult and was invariably accompanied by decomposition.

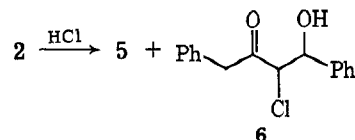


The reactions of a similar type of diazo ketone with a carbon-hydrogen bond adjacent to the diazo carbon but without the hydroxy group have been studied under pyrolytic and photolytic conditions.⁶ The exclusive or the major product in these reactions resulted from an apparent 1,2-hydride shift to form an α,β -unsaturated ketone; the Wolff rearrangement product was formed in small amounts in some cases (reaction 1). In view of the moderate yields of the

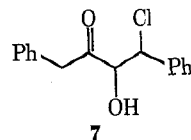


dione **5** and the incomplete characterization of the reaction mixture, it would be difficult to eliminate Wolff rearrangement as a reaction path. No evidence for a β -lactone or ester, however, could be adduced from the spectra of the crude reaction mixture; therefore, the Wolff rearrangement must certainly be a minor reaction path. Thus, the presence of a hydroxy group α to the diazo group does not change the general reactivity observed for diazoalkyl ketones.

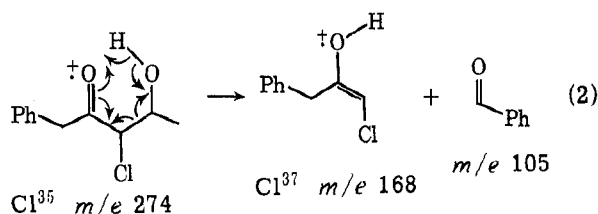
Hydrogen Halide.—Treatment of a solution of diazo ketone **2** in ether with dry hydrogen chloride gas, evaporation of the solvent, and preparative tlc of the concentrate gave a 20% yield of dione **5** and a 31% yield of 3-chloro-1,4-diphenyl-4-hydroxy-2-butanone (**6**).



The ir spectrum of **6** contained bands at 2.93 and 5.88 μ for the hydroxyl and the keto groups, respectively. The nmr spectrum, besides a multiplet at δ 7.18 and a singlet at δ 3.77 due to ten phenyl and two methylene protons, respectively, revealed a rough quartet at δ 4.86 ($J = 5$, $J' = 8$ Hz) attributed to a benzylic methine proton, and doublets at δ 4.24 ($J' = 8$ Hz) and 3.30 ($J = 5$ Hz) assigned to the methine proton α to the keto group and hydroxyl proton, respectively. When the nmr sample was treated with D_2O , the doublet at δ 3.30 disappeared and the quartet at δ 4.86 collapsed to a doublet, confirming these assignments. It is not possible to assign structure **6** to the chloro hydroxy ketone exclusively on the basis of ir and nmr spectra, because the isomeric structure **7** is also compatible with the spectral data. Evidence in favor of



structure **6** came from the mass spectra of the chloro compound, which, in addition to an m/e 274 (M^+) and other peaks, had important peaks at m/e 168 and 170 in *ca.* 3:1 ratio, indicating the presence of ^{35}Cl and ^{37}Cl in the ions, respectively. McLafferty rearrangement⁷ of **6** readily accounts for these peaks (reaction 2) but a reasonable cleavage of **7** to give the observed halogen containing fragments is not possible.



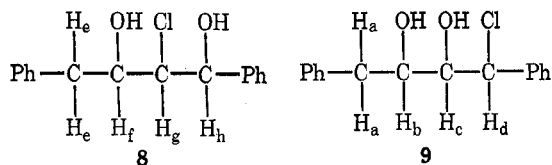
Unambiguous proof for the assignment of the structure **6** to the HCl reaction product was obtained from the nmr spectrum of the reduction product of **6** with LiAlH_4 . LiAlH_4 reduction of **6** gave a 46% yield of 3-chloro-1,4-diphenyl-1,3-butanediol (**8**). The ir spectrum showed no carbonyl peak and the compound gave a negative borax test for a 1,2-diol. The nmr spectrum of **8** revealed a ten-proton multiplet at δ 7.27, a rough one-proton multiplet at δ 4.98, a two-proton multiplet at δ 3.97, a rough one-proton doublet at δ 3.57, and a three-proton multiplet at δ 2.84. On addition of a drop of deuterium oxide, the multiplet at δ 4.98 became a sharp doublet, the doublet at δ 3.57 disappeared, and the multiplet at δ 2.84 integrated for two protons. This deuterium exchange established three things: (a) the peak at δ 3.57 was due to a

(5) T. Severin and H. Lercher, *Ber.*, **103**, 2148 (1970).

(6) V. Franzen, *Justus Liebig's Ann. Chem.*, **602**, 199 (1957).

(7) V. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

hydroxyl proton; (b) the second hydroxyl proton was under the multiplet at δ 2.84; and (c) the peak at δ 4.98 was due to a proton which was on a carbon bearing a hydroxyl group. The last point confirmed the structure of the reduced product as **8** and, therefore, of the structure of the starting chlorohydroxy ketone as **6**.



Structure **9**, which would be expected from the reduction of **7**, would have two protons on carbon atoms bearing a hydroxyl group, *i.e.*, protons H_b and H_c . The nmr spectrum of **9** in deuterium oxide would be expected to show multiplet for the proton H_b , since it would be coupled to the methylene protons H_{aa} as well as to the methine proton H_c . Similarly, H_c would be expected to give a multiplet (a quartet, or a triplet) because it would be coupled to the two neighboring methine protons H_b and H_a . The proton appearing at δ 4.98 which must be coupled to a hydroxyl group, however, was only a doublet and, therefore, could not be due to either H_b or H_c . This excluded the 1,2-diol **9** from consideration as the possible structure for the reduction product and, therefore, eliminated structure **7** as the possible structure for the chlorohydroxy ketone.

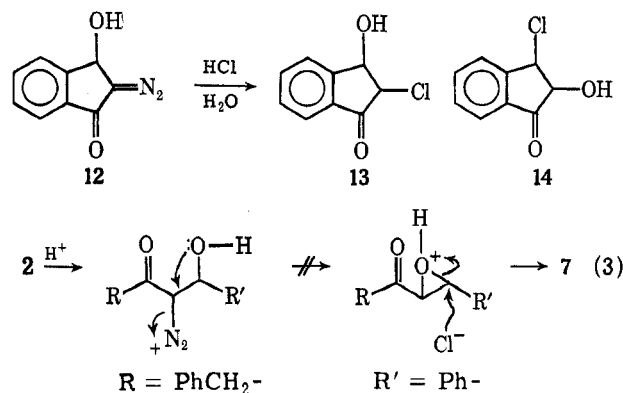
Structure **8**, the product which would be expected from the reduction of **6**, would also have two protons on carbon bearing a hydroxyl group, *i.e.*, protons H_f and H_h . Once again, H_f would be expected to give a multiplet, since it would be coupled to the methylene protons H_{ee} as well as to the methine proton H_g . H_f could, therefore, absorb at either δ 2.84 or δ 3.97 (probably the latter) but cannot be the cause of the doublet at δ 4.98. However, the proton H_h is coupled only to the methine proton H_g and would be expected to give a doublet after deuteration of the alcohol. The doublet at δ 4.98 must be, therefore, due to proton H_h . This firmly established the structure **8** for the reduced product and, therefore, structure **6** for the chlorohydroxy ketone.

An exactly comparable set of reactions was carried out with the hydroxydiazoketone **2** and anhydrous hydrogen bromide in ether to give 3-bromo-1,4-diphenyl-4-hydroxy-2-butane (**10**) in 45% yield and the dione **5** in 10% yield. $LiAlH_4$ reduction of **10** gave 2-bromo-1,4-diphenyl-1,3-butanediol (**11**). Their ir, nmr, and mass spectral data in this series of compounds (see Experimental Section) was entirely consistent with the structures assigned in the chlorohydroxy ketone series.

Treatment of **12** with aqueous hydrochloric acid solution has been reported⁵ to give **13**, although the evidence for this structure is not compelling. An nmr structure determination suffers from an inability to distinguish **13** from **14**. In this as well as our series this type of product could have arisen from anchimerically assisted loss of nitrogen by the adjacent hydroxyl group from a diazonium intermediate to form an intermediate or transient epoxide (reaction 3). Acidic opening of the epoxide would favor formation of **7**.

Since **7** was not formed, however, we feel confident in eliminating this reaction path and in concluding that the intramolecular hydroxyl group cannot compete with chloride or bromide ion for the intermediate diazonium ion.

The hydride shift which evidently is necessary to form the dione **5** in acid need not be assisted by the hydroxyl group because α,β -unsaturated ketones are formed on hydrogen halide treatment of alkyl diazo ketones.⁸ It is not clear why 1,3-indandione is not formed from **12** on acid treatment. The aqueous conditions of this reaction or some stereochemical factor could be involved, and these and other possibilities are under investigation.



Experimental Section

Irradiations were carried out with a 550-W Hanovia 673A-36 medium pressure mercury-vapor arc lamp in a Pyrex reaction vessel equipped with a Pyrex, water cooled, immersion well, a nitrogen inlet, and a magnetic stirrer. Analytical tlc was performed with silica gel HF-254 or aluminum oxide H (Merck). Melting points were determined on a K \ddot{o} fler hot stage and are uncorrected.

The infrared (ir) spectra were determined on a Beckman IR-12 spectrometer. The nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer using TMS as an internal reference. The mass spectra were obtained on a CEC 491 mass spectrometer at 70 eV.

3-Diazo-1,4-diphenyl-4-hydroxy-2-butanone (2).—To an ice cold, stirred solution of 1.0 g (6.0 mmol) of 1-diazo-3-phenyl-2-propanone⁹ (**1**) in 60 ml of redistilled ethanol (0.10 *M*) and 3 ml of benzaldehyde was added 0.1 g of sodium hydroxide in 5 ml of water. After 30 min of stirring, during which time the solution acquired a golden yellow color, another 0.1 g of sodium hydroxide in 5 ml of water and 3 ml of benzaldehyde were added. The solution was stirred for 2 hr more and then poured into 150 ml of cold water and finally extracted with three 100-ml portions of carbon tetrachloride. After evaporation of most of the solvent, the yellow extract was placed on a chromatography column (24 mm by 34 cm) packed with basic alumina (Fisher, 100 g) in carbon tetrachloride and eluted with carbon tetrachloride (150 ml), benzene (150 ml), and finally ethanol (300 ml). Removal of the solvent from the ethanol fraction afforded 1.4 g of yellow oil, which was crystallized in cold ether-pentane to give 1.2 g (65%) of 3-diazo-1,4-diphenyl-4-hydroxy-2-butanone (**2**) as yellow crystals: mp 56–57°; nmr (CCl_4) δ 7.21 (m, 10 H, 2 Ph), 5.91 (d, 1 H, $J = 4$ Hz, CHOH), 4.20 (d, 1 H, $J = 4$ Hz, CHOH), 3.68 ppm (s, 2 H, CH_2); nmr (CCl_4-D_2O) δ 7.20 (d, 10 H, 2 Ph), 5.88 (s, 1 H, CHOD), 3.66 ppm (s, 2 H, CH_2); ir (KBr) 2.94 (w, OH), 4.78 (s, CHN_2), 6.08 μ (s, CO). *Anal.* Calcd for $C_{16}H_{14}N_2O_2$: C, 72.20; H, 5.26; N, 10.52. Found: C, 72.30; H, 5.31; N, 10.40.

Irradiation. A. In Benzene.—A solution of 500 mg (1.9 mmol) of the hydroxydiazoketone **2** in 150 ml of benzene was

(8) E. M. Avaro and J. Levisalles, *Bull. Soc. Chim. Fr.*, 735 (1967).

(9) A. Platner and H. Heusser, *Helv. Chim. Acta*, **28**, 1046 (1945).

purged with nitrogen for 30 min and then irradiated through Pyrex for 75 min. Removal of the solvent under reduced pressure gave a yellow oil which was dissolved in 4 ml of methanol, poured into 20 ml of a hot saturated solution of aqueous copper acetate, and left overnight. Filtration gave green flakes of the copper salt of 1,4-diphenyl-1,3-butanedione which were washed with cold ether and dried, mp 198–200° (lit.¹⁰ mp 200–201°). The copper salt was placed in a 125-ml separatory funnel together with 10 ml of ether and was shaken with 20-ml portions of 20% sulfuric acid until decomposition was complete and two homogeneous phases were present. The ether layer was dried over Drierite, filtered, and evaporated to give 220 mg (49%) of 1,4-diphenyl-1,3-butanedione (5) as yellow crystals: mp 52–53° (lit.¹⁰ mp 52°); nmr (CCl₄) δ 15.50 (s, 1 H, CHO), 7.75 and 7.25 (m, 10 H, 2 Ph), 6.02 (s, 1 H, CHO), 3.59 ppm (s, 2 H, CH₂CO); ir (CHCl₃) 3.64 (broad m, OH), 6.41 μ (broad s, CO).

B. In Methanol.—Irradiation of 500 mg (1.9 mmol) of the diazo ketone 2 in 150 ml of methanol for 75 min followed by the same work-up procedure as above gave 235 mg (52%) of the dione 5, mp 52–53°.

Pyrolysis of 2.—A stirred solution of 500 mg (1.9 mmol) of the diazo ketone 2 in 20 ml of redistilled chlorobenzene under a reflux condenser was heated rapidly in a preheated oil bath maintained at 170°. After about 60 sec, vigorous evolution of nitrogen occurred and was complete in approximately 5 min. Treatment of the yellow oil, formed on evaporation of the solvent, with a hot saturated aqueous solution of copper acetate and decomposition of the precipitated copper salt in a similar fashion as in the photolysis reactions gave 200 mg (40%) of the dione 5, mp 52–53°.

3-Chloro-1,4-diphenyl-4-hydroxy-2-butanone (6).—Dry hydrogen chloride gas was bubbled through a stirred solution of 500 mg (1.9 mmol) of hydroxy diazo ketone 2 in 60 ml of anhydrous ether. After 10 min, the light yellow reaction solution was washed with three 20-ml portions of 2% sodium bicarbonate solution. Removal of the solvent afforded a light yellow oil which was subjected to preparative thin layer chromatography on silica gel developed with chloroform. Removal of the spot with *R_f* 0.69, extraction with ether, and subsequent evaporation of the solvent yielded 220 mg of a light orange liquid which crystallized in ether–pentane to give 90 mg (20%) of brown crystals of dione 5, mp 52–53°. Similarly, recovery of the spot with *R_f* 0.45 gave 230 mg of a brown oil which crystallized in ether–pentane to give 160 mg (31%) of 3-chloro-1,4-diphenyl-4-hydroxy-2-butanone (6) as white crystals: mp 51–52°; nmr (CCl₄) δ 7.18 (m, 10 H, 2 Ph), 4.86 (q, 1 H, *J* = 5, *J'* = 8 Hz, CHO), 4.24 (d, 1 H, *J'* = 8 Hz, CHCl), 3.77 (s, 2 H, CH₂), 3.30 ppm (d, 1 H, *J* = 5 Hz, CHO); ir (KBr) 2.93 (w, OH), 5.88 μ (s, CO); mass spectrum (70 eV, 90°) *m/e* (rel intensity) 276 (0.19), 274 (0.44), 170 (5), 168 (18), 119 (10), 107 (8), 106 (23), 105 (28), 92 (10), 91 (100), 78 (19), 77 (48), 65 (24), 51 (30), 50 (16), 39 (21). *Anal.* Calcd for C₁₈H₁₅ClO₂: C, 69.96; H, 5.46; Cl, 12.93. Found: C, 69.76; H, 5.51; Cl, 13.05.

3-Bromo-1,4-diphenyl-4-hydroxy-2-butanone (10).—Following the same procedure as for the preparation of 6, treatment of 500

mg (1.9 mmol) of hydroxy diazo ketone 2 with hydrogen bromide gas gave on work-up a light yellow oil which was dissolved in 2 ml of ether and 10 ml of pentane and cooled in a refrigerator for 48 hr to give 280 mg (45%) of 3-bromo-1,4-diphenyl-4-hydroxy-2-butanone (10) as white crystals: mp 56–57°; nmr (CCl₄) δ 7.19 (m, 10 H, 2 Ph), 4.95 (q, 1 H, *J* = 5, *J'* = 8 Hz, CHO), 4.32 (d, 1 H, *J'* = 8 Hz, CHBr), 3.85 (s, 2 H, CH₂), 3.40 ppm (d, 1 H, *J* = 5 Hz, CHO); ir (KBr) 2.94 (w, OH), 5.93 μ (s, CO); mass spectrum (70 eV, 90°) *m/e* (rel intensity) 320 (0.4), 318 (0.4), 239 (8), 214 (13), 212 (12), 147 (11), 133 (15), 131 (19), 119 (8), 107 (19), 106 (17), 105 (19), 103 (13), 92 (14), 91 (100), 75 (11), 73 (30), 65 (20), 51 (19), 39 (11). *Anal.* Calcd for C₁₈H₁₅BrO₂: C, 60.23; H, 4.70; Br, 25.04. Found: C, 60.42; H, 4.51; Br, 25.29.

Work-up of the remainder of the reaction mixture by the copper salt method gave 30 mg (10%) of the dione 5, mp 52–53°.

2-Chloro-1,4-diphenyl-1,3-butanediol (8).—A solution of 100 mg (0.36 mmol) of chloro hydroxy ketone 6 in 5 ml of anhydrous ether was added dropwise to a stirred suspension of 40 mg of LiAlH₄ in 10 ml of anhydrous ether. After stirring for 1 hr, excess LiAlH₄ was decomposed with 3 ml of ethyl acetate, and the reaction mixture was filtered to remove inorganic salts. The filtrate, which still contained a small amount of inorganic salts, was stripped of the solvent and the residue was extracted with ether. Evaporation of the solvent from the extract gave a colorless, viscous oil which was crystallized from ether–pentane to give 46 mg (46%) of 2-chloro-1,4-diphenyl-1,3-butanediol (8): mp 88–89°; nmr (CDCl₃) δ 7.27 (m, 10 H, 2 Ph), 4.98 (m, 1 H, CHO), 3.97 (m, 2 H), 3.57 (d, 1 H, *J* = 5 Hz, OH), 2.84 ppm (m, 3 H); nmr (CDCl₃-D₂O) δ 7.27 (m, 10 H, 2 Ph), 4.98 (d, 1 H, *J* = 5 Hz), 3.97 (m, 2 H), 2.84 ppm (m, 2 H). *Anal.* Calcd for C₁₈H₁₇ClO₂: C, 69.43; H, 6.15; Cl, 12.84. Found: C, 69.35; H, 6.10; Cl, 13.02.

2-Bromo-1,4-diphenyl-1,3-butanediol (11).—The LiAlH₄ reduction of 100 mg (0.31 mmol) of 10 was carried out in the same manner as for 6 to yield 42 mg (42%) of 2-bromo-1,4-diphenyl-1,3-butanediol (11): mp 106–107°; nmr (CDCl₃) δ 7.28 (m, 10 H, 2 Ph), 5.10 (m, 1 H, CHO), 4.05 (m, 2 H), 3.40 (d, 1 H, *J* = 5 Hz, OH), 2.85 ppm (m, 3 H); nmr (CDCl₃-D₂O) 7.28 (m, 10 H, 2 Ph), 5.10 (d, 1 H, *J* = 5 Hz, CHO), 4.05 (m, 2 H), 2.85 ppm (m, 2 H). *Anal.* Calcd for C₁₈H₁₇BrO₂: C, 59.85; H, 5.29; Br, 24.91. Found: C, 60.13; H, 5.58; Br, 24.90.

Registry No.—2, 34737-54-7; 5, 3442-15-7; 6, 34737-56-9; 8, 34737-57-0; 10, 34737-58-1; 11, 34737-59-2.

Acknowledgment.—We are indebted to the National Science Foundation (Grant GP-28407) for financial aid in the purchase of the mass spectrometer.

(10) L. I. Smith and R. E. Kelly, *J. Amer. Chem. Soc.*, **74**, 3300 (1952).