

98760-51-1; IIc, 93159-17-2; IIIa, 86646-86-8; IIIb, 84574-05-0; IIIc, 87207-96-3; IIId, 26172-18-9; IVa, 50869-01-7; IVb, 50869-02-8; IVc, 86646-85-7; V, 98760-52-2; VIa, 2431-91-6; VIb, 53651-61-9; VIc, 19587-93-0; VIId, 2819-86-5; VIe, 3238-38-8; VIf, 527-60-6; VIg, 527-35-5; VIh, 576-26-1; VIIa, 489-01-0; VIIb, 128-37-0; VIIc, 128-39-2; δ -T, 119-13-1; γ -T, 54-28-4; β -T, 16698-35-4; α -T, 59-02-9; DMT, 17976-95-3; 2-methyl-2-propen-1-ol, 513-42-8; 6-hydroxy-5,7,8-trimethylguanine, 50869-00-6; 6-hydroxy-5,7,8-trimethyltetrahydroquinolinium tri-

fluoroacetate, 98760-53-3; 4-mercaptotrimethylphenol, 85460-73-7; 3-methyl-2-buten-1-ol, 556-82-1; trimethylhydroquinone, 700-13-0; styrene, 100-42-5.

Supplementary Material Available: Tables VI-XXI giving detailed X-ray crystallographic data, final parameters, and structural factor lists (70 pages). Ordering information is given on any current masthead page.

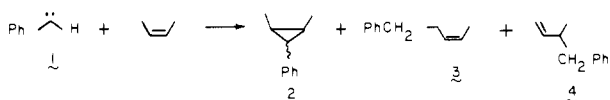
The Formation of an Enantiomerically Pure Product of Free Radical Coupling. The Chemistry of Diphenylcarbene in Polycrystalline (S)-(+)-2-Butanol¹

José Zayas and Matthew S. Platz*²

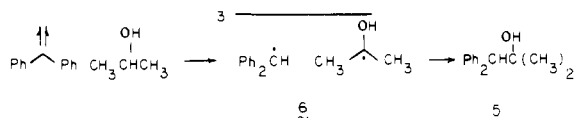
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received February 19, 1985

Abstract: Photolysis of 0.1 M diphenyldiazomethane at 77 K or 137 K in solid (S)-(+)-2-butanol gives tertiary alcohol **9** along with other products. Compound **9** was isolated and found to be enantiomerically pure by chiral NMR shift reagents. Compound **9** is formed by reaction of triplet diphenylcarbene with (S)-(+)-2-butanol to give a radical pair which subsequently collapses. The solid-state matrix directs the radical pair collapse with complete retention of configuration.

In 1971 Moss and Dolling discovered that the photochemical generation of arylcarbenes in low-temperature solids enhances the yield of triplet-derived products.³ Phenylcarbene **1** reacts with *cis*-2-butene in solution to give >85% of cyclopropanes **2** (syn and anti) and only a small (<15%) amount of olefins **3** and **4**. In the solid state (-196 °C) the yield of **3** plus **4** exceeds 50% and the yield of **2** drops below 50%.



In subsequent years several more examples of the unusual solid-state chemistry of arylcarbenes have been reported by Moss,⁴ Tomioka,⁵ and Platz.⁶ Tomioka discovered that diphenylcarbene (DPC) reacts with 2-propanol in the solid state to give high yields of alcohol **5**, presumably by hydrogen atom abstraction by triplet DPC to give radical pair **6**. In solution phase only trace amounts



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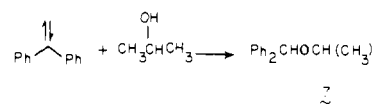
Table I. Absolute Yield ($\pm 2\%$) of Products Formed by the Reaction of DPC with D,L-2-Butanol and (S)-(+)-2-Butanol at 77 K

product	absolute yield (%)	
	D,L-2-butanol	(S)-(+)-2-butanol
8	6	6
9	12	13
10	5	6
11	1	1
12	1	1
13	11	10
total	36	37

Table II. Absolute Rate of Decay of Triplet DPC in D,L- and (S)-(+)-2-Butanol at 98 K (Three Trials Each)

D,L k ($s^{-1/2}$)	(S)-(+) k ($s^{-1/2}$)
2.96×10^{-2}	2.69×10^{-2}
2.73×10^{-2}	2.50×10^{-2}
2.60×10^{-2}	2.80×10^{-2}
av $2.8 \pm 0.2 \times 10^{-2}$	av $2.7 \pm 0.2 \times 10^{-2}$

of **5** are formed, the near exclusive product being ether **7** derived from reaction of singlet DPC with solvent. It occurred to us that

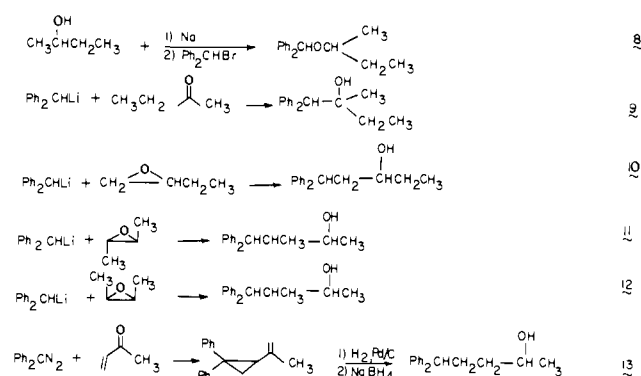


if a chiral alcohol were employed as a polycrystalline matrix then a radical pair (such as **6**) would again be formed. The rigid polycrystalline environment should prevent rotational motion of the components of the radical pair and direct their collapse to form a stable product in only one sense to give an enantiomerically enriched material. As described in the next section these expectations were confirmed in the diphenylcarbene-2-butanol system.

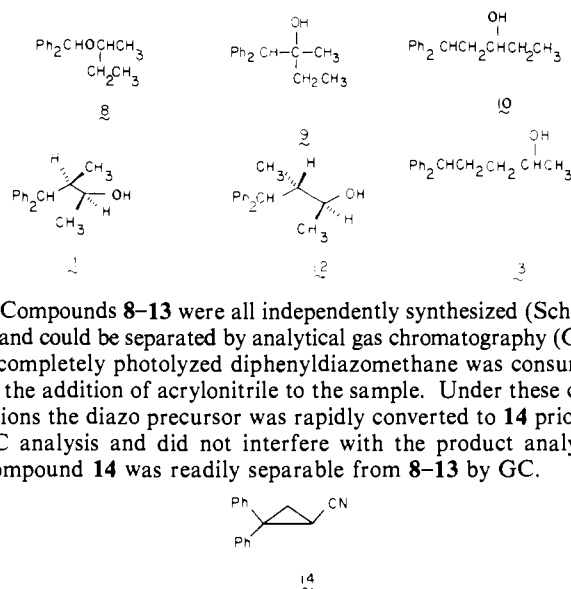
Results

The DPC-2-butanol system was chosen based upon Tomioka's results and the accessibility of enantiomerically pure (S)-(+)-2-

Scheme I



butanol. The products expected from the reaction of DPC with 2-butanol are **8**–**13**.



Compounds **8**–**13** were all independently synthesized (Scheme I) and could be separated by analytical gas chromatography (GC). Incompletely photolyzed diphenyldiazomethane was consumed by the addition of acrylonitrile to the sample. Under these conditions the diazo precursor was rapidly converted to **14** prior to GC analysis and did not interfere with the product analysis. Compound **14** was readily separable from **8**–**13** by GC.

Photolysis of 0.1 M diphenyldiazomethane in D,L-2-butanol and (S)-(+)-2-butanol at 77 K gave the product distributions listed in Table I. The yields are absolute and not corrected for incomplete photolysis of diphenyldiazomethane. The kinetics of triplet DPC (as measured by EPR at 98 K) are listed in Table II in units of $s^{-1/2}$.⁷ For our purposes it is suffice to say that triplet DPC decayed at the same rate in D,L and (S)-(+)-2-butanol at 98 K. The units of $s^{-1/2}$ are used merely for convenience. The decay of carbenes (and of radicals⁸ and excited states⁹) in polycrystalline solids is nonexponential due to nonequivalent sites in the matrix. In previous work it was empirically determined that plots of $\ln[\text{carbene}]$ vs. $\text{time}^{1/2}$ gave reasonable straight lines over 2–3 half-lives.⁷ A matrix distribution of sites mode has been advanced which justifies this time dependence.¹⁰ The “rate constant” in $s^{-1/2}$ should not be taken as a true rate constant for an elementary process, it is used because it is the most precise way of reporting the data.

The chemical fingerprints of DPC and (S)-(+)-2-butanol at 77 K were also identical (Table I). The chemical and kinetic results were not foregone conclusions as the local environment about matrix-isolated DPC in solid D,L and (S)-(+)-2-butanol need not have been equivalent and could have differentially influenced the chemistry and kinetics of DPC.

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Table III. The Absolute Yields ($\pm 3\%$) of Products from Reaction of DPC with D,L-2-Butanol as a Function of Temperature

product	temperature (K)							
	199	173	159 ^a	153	137	120	102	102 ^b
8	79	66	46	38	32	16	10	9
9	2	2	51	46	62	20	18	2
13					1	36	36	27
10					1	8	9	
total	81	68	97	84	96	80	75	38

^aMelting point of pure D,L-2-butanol. ^bD,L-2-Butanol-2-d.

Table IV. Absolute Yields of Products Derived from the Reaction of DPC with D,L-2-Butanol as a Function of Diphenyldiazomethane Concentration at 77 K

product	concentration (M)			
	0.025	0.05	0.1	0.1 ^a
8	12	7	6	9
9	38	16	12	14
13	14	10	10	10

^aThe sample was stored for 18 h at 77 K in the dark following photolysis before thawing.

The product distributions obtained in D,L-2-butanol at various temperatures are given in Table III. In solution at 173 and 199 K the near exclusive product is ether **8**, the singlet reaction product. Only trace amounts of tertiary alcohol **9** were present. At the melting point of pure D,L-2-butanol (159 K) there is a dramatic change in the product mixture. At this temperature tertiary alcohol **9** is formed in 51% yield. Photolysis at 137 K gives the best absolute yield (62%) of **9** and it is formed in nearly twice the yield of ether **8** at this temperature. Tertiary alcohol **9** is the key product in this study since it is the product of reaction of DPC with the chiral center. Photolysis of diphenyldiazomethane at 120 K gives a more complex mixture than observed in D,L-2-butanol polycrystals at higher temperatures. Significant amounts of **10** and **13** are formed at 120, 102, and 77 K.

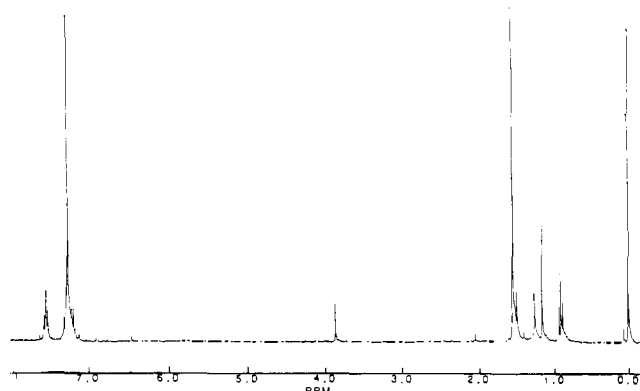
There is a clear break in the product distribution observed in polycrystalline D,L-2-butanol in the temperature range 159–137 and 120–77 K. We believe this represents a change in the “rigidity” of solid D,L-2-butanol. Between 159 and 137 K, DPC must have enough mobility in the solid to distinguish the various CH bonds of D,L-2-butanol. Between 77 and 120 K DPC is probably held more rigidly in the solid and can only react with whichever CH bond is closest. Between 137 and 159 K DPC has enough freedom of motion in the polycrystal to preferentially abstract the weakest CH bond (the tertiary CH) of the matrix to give the most stable radical pair and ultimately **9**. Between 77 and 120 K the motion available to matrix-isolated DPC is much more restricted. At these temperatures the chemistry of DPC is determined by the closest CH bond in the rigid matrix. This will obscure the chemical selectivity displayed by DPC at higher temperatures (137–159 K) where the carbene is more mobile. This effect leads to enhanced CH abstraction–recombination at a primary CH bond to ultimately give **13**.

Photolysis of diphenyldiazomethane in D,L-2-butanol-2-d (obtained by reduction of 2-butanone with lithium aluminum deuteride) reduces the yield of tertiary alcohol **9** by nearly an order of magnitude at 102 K. A kinetic isotope effect on the decay of triplet DPC of 1.3 at 102 K was observed ($k(\text{D,L-2-butanol}) = 4.27 \pm 0.12 \times 10^{-2} \text{ s}^{-1/2}$; $k(\text{D,L-2-butanol-2-d}) = 3.26 \pm 0.01 \times 10^{-2} \text{ s}^{-1/2}$).

Several photolyses were performed as a function of concentration of diphenyldiazomethane at 77 K (Table IV). The percentage yields of adducts **8**, **9**, and **13** generally increase as the concentration of the diazo precursor decreases. At the higher concentrations it is not possible to effect an efficient conversion of diazo compound to DPC. Photolyses were also performed at 0.2, 0.3, and 0.4 M. Under these conditions very low yields of adducts were obtained as well as several unidentified compounds and some tetraphenylethylene. Solutions of 0.1 M diazo compound appear to be the best concentration for the preparation of carb-

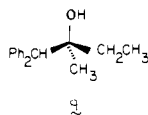
Table V. The Amounts of $\text{Eu}(\text{DCM})_3$ Added to NMR Samples of Compound **9** (See Figure 2)

	run	$\text{Eu}(\text{DCM})_3$, mg (total amount)
(I)	racemic	9
	A	0
	B	5.7
	C	11.7
(II)	preparative	9 (77 K)
	A	0
	B	6.2
	C	12.3
(III)	preparative	9 (137 K)
	A	0
	B	5.4
	C	10.9
	D	16.8

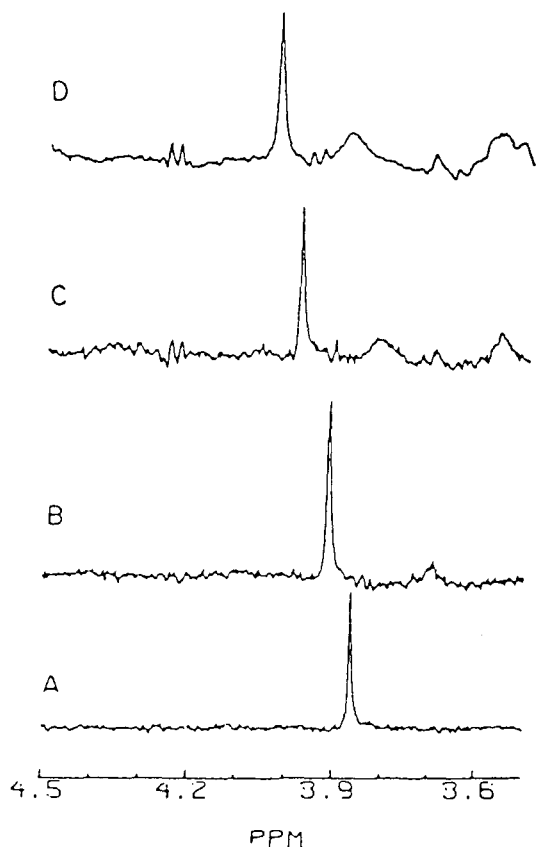
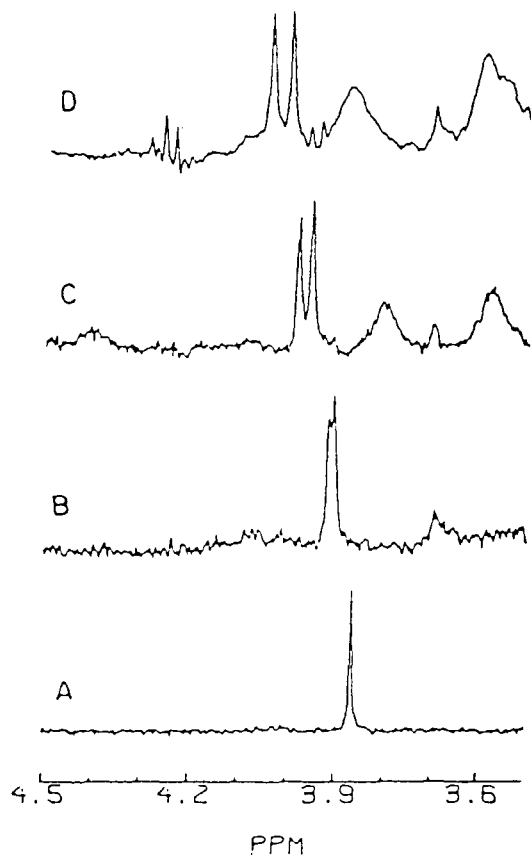
**Figure 1.** The NMR spectrum of (*S*)-**9** obtained from reaction of DPC with (*S*)-2-butanol at 77 K. The singlet at δ 1.5 is residual water.

ene-*D,L*-2-butanol adducts. It was also determined that allowing the sample to stand in the dark for 18 h at 77 K following irradiation of diphenyldiazomethane does not affect the product distribution. This demonstrates that the adducts are formed in the matrix and not upon thawing the sample, as EPR spectroscopy has shown that triplet DPC decays completely within 18 h in the matrix. Experiments were also performed in frozen mixtures of benzene and *D,L*-2-butanol. Kinetic EPR work with DPC has demonstrated that DPC reacts very slowly with benzene at 77 K, although one cannot predict the mode of crystallization of such a solvent mixture. Photolysis of 0.1 M diphenyldiazomethane in 1:1 *D,L*-2-butanol:benzene led to inefficient photolysis of the diazo compound and very low yields of adducts. Unfortunately it would not be possible to decrease the amount of (*S*)-(+)-2-butanol needed in preparative experiments (*vide infra*).

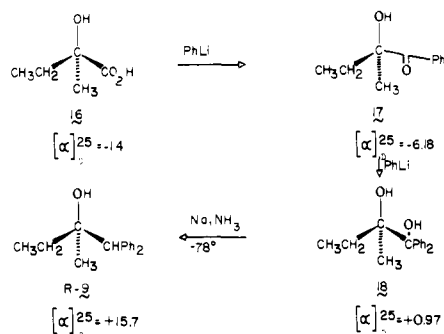
Preparative experiments were performed with 1.0 mL of a 0.1 M solution of diphenyldiazomethane in (*S*)-(+)-2-butanol. These solutions were photolyzed in separate experiments at 77 and 137 K. Approximately 3–4 mg of tertiary alcohol **9** could be separated from the reaction mixture by medium-pressure liquid chromatography. Compound **9** was found to be optically active with specific rotations of $[\alpha]^{25}_{\text{D}} -9.76$ (*c* 0.72, CCl_4) (77 K photolysis) and $[\alpha]^{25}_{\text{D}} -10.8$ (*c* 0.25, CCl_4) (137 K photolysis).



The NMR spectrum of **9** is shown in Figure 1. The optical purity of preparative samples of **9** was analyzed by monitoring the benzydryl resonance of **9** at δ 3.85 in the presence of the chiral shift reagent, tris(*d,d*-dicampholylmethanato)europium(III), ($\text{Eu}(\text{DCM})_3$)¹¹ (**15**).

**Figure 2.** The benzydryl proton of tertiary alcohol **9** obtained from reaction of DPC with *D,L*-2-butanol (top) and (*S*)-2-butanol (bottom) at 77 K in the presence of ≈ 0 mg (A), 5 mg (B), 10 mg (C), and 15 mg (D) of chiral shift reagent.

Scheme II

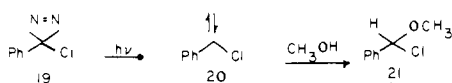


As can be seen from Figure 2 the tertiary alcohol **9** formed in (*S*)-(+)-2-butanol polycrystals at 137 and 77 K is enantiomerically pure within our limits of detection.¹

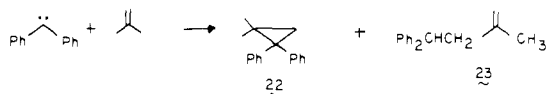
We expected that alcohol **9** would be formed with retention and have the *S* configuration. To establish the configuration of preparative **9**, it was resynthesized by an independent route of known configuration. Hydroxy acid **16** can be resolved into its enantiomerically pure components. The absolute configurations of the dextro- and levorotamers have been established.¹² For synthetic reasons the levorotatory acid **16** was converted into *R* tertiary alcohol **9** as shown in Scheme II. The *R* alcohol **9** has $[\alpha]^{25}_D +15.7$. The authentic *R* alcohol **9** has a rotation opposite to the matrix-prepared **9**, establishing the latter material as *S*, the product of retention.

Discussion

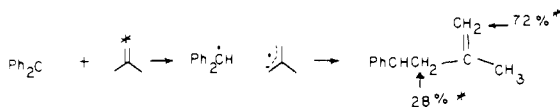
A trivial explanation of the enantiomerically pure reaction to form **9** between DPC and (*S*)-(+)-2-butanol is that it is a concerted singlet state reaction. Kirmse and Buschhoff have shown that singlet methylene inserts into a CH bond of paraldehyde with greater than 95% retention.¹³ In this view singlet DPC reacts completely by OH insertion in solution but by both OH and CH insertion in solids. Perhaps this matrix effect could be explained by hydrogen bonding between the hydroxyls in the solid state rendering the OH bond inaccessible. However, there is a counter example to this view in the literature. Tomioka has photolyzed phenylchlorodiazirine **19** in methanol solution and in frozen solids.⁵ The photolytically generated phenylchlorocarbene **20** reacts only by OH insertion to give **21** in both the liquid and solid state. No matrix effect operates on an authentic ground-state singlet carbene to give CH insertion with an alcohol.



The singlet explanation also ignores the work of Moss, who studied the reaction of DPC with isobutene.⁴ At 273 K the ratio of **23** to **22** is 0.243, but it becomes 44.6 at 77 K. When labeled

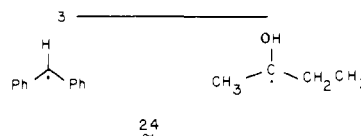


olefin is used, the distribution of the label is consistent with an allylic radical intermediate. Surely the enhanced product of formal CH insertion **23** must have at least a partial triplet carbene component.



In light of the work of Tomioka and Moss we believe that tertiary alcohol **9** is largely derived from triplet DPC. If the

singlet-triplet free-energy separation in DPC is as large as 3 kcal/mol as has been reported¹⁴ the ratio of singlet to triplet DPC at equilibrium at 77 K is less than 10^{-7} . We do not feel it is likely that singlet DPC will react with the 2-butanol matrix prior to equilibration with the triplet. Eisenthal has determined that the intersystem crossing (isc) lifetime of singlet DPC is 110 ps at 298 K.¹⁵ The isc rate should not substantially diminish as the temperature is decreased.¹⁶ In fact Doetschmann has shown that isc is complete in less than 100 ns at 1.2 K.¹⁷ It is hard to believe that singlet DPC can react this rapidly with the matrix at 77 K. Furthermore a very intense EPR signal of triplet DPC can be observed on photolysis of 0.1 M diphenyldiazomethane in *D,L*-2-butanol. The weight of the evidence points to substantial involvement of triplet DPC in the formation of **9**. This requires the intermediacy of radical pair **24**. The radical pair must be



chiral even though the individual components of the pair will be achiral in their most stable conformations. The solid state prevents rotational motion of the individual radicals and directs the radical pair collapse with retention of configuration. This observation is not unprecedented. According to Schmidt and Cohen's "Topochemical Principle" solid-state reactions will occur with minimal molecular motion.¹⁸ Several examples of enantioselective syntheses in single crystals have been reported.¹⁹ To our knowledge this represents the first such example in a frozen solid of unknown composition.

Experimental Section

EPR Measurements: EPR measurements were made with a Varian E-112 X-band EPR spectrometer equipped with a modified microwave cavity which admitted light through a series of louvers on one side. Carbene spectra were obtained after three freeze-pump-thaw cycles to remove traces of oxygen.

Kinetics were obtained as previously described.⁷ All kinetic measurements were obtained as a minimum of two and typically three trials. Irradiation of EPR samples was accomplished with a Schoeffel 1000-W high-pressure Hg-Xe lamp. A water-cooled aqueous CuSO_4 filter (Pyrex, 0.1 M, 2 cm path length) was used to remove ultraviolet and infrared radiation.

Procedure for Photolysis in Racemic and Enantiomerically Pure Matrices at 77 K. A 1.0-mL aliquot of an approximately 0.1 M solution of diphenyldiazomethane in *D,L*- or (*S*)-(+)-2-butanol is placed in three 4-mm Pyrex tubes washed with ammonium hydroxide and oven-dried prior to use. Each Pyrex tube contained a sealed capillary tube inside. This exposed more of the solid solution to light thereby shortening the photolysis time. The samples were sealed under vacuum after 3 freeze-pump-thaw cycles. The usual photolysis time was 5 to 6 h at 77 K with use of an apparatus equipped with two Rayonet RPR 3500 lamps (3500 Å). The tubes were removed every 1 to 1.5 h and thawed in the dark, then they were frozen again and photolyzed.

After the photolysis was complete the samples were transferred rapidly to a storage dewar containing liquid nitrogen where they were allowed to stand overnight (usually 16–20 h). The samples were then thawed and excess acrylonitrile was added to consume any unreacted diazo compound. The excess alcohol and acrylonitrile were removed under reduced pressure (0.1 mmHg/80 °C).

Separation of 1,1-diphenyl-2-methylbutan-2-ol (**9**) was accomplished by means of medium-pressure liquid chromatography (MPLC) with the

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following conditions: eluent, 2.5% ethyl acetate/hexane; flow, 6 mL/min (pump = 2 div.); Collector, 75 s/sample; column size, (240–10) Li-Chroprep Si60 EM Reagents.

The amount of the diphenylmethyl alcohol **9** isolated was approximately 3 mg in each case. It showed mostly one spot on TLC (silica) R_f under identical conditions, both were also compared by GC/MS. Synthetic **9** and **9** derived from matrix reactions had the same spectra obtained on a Finnigan 4021 with use of a 6 ft \times 1/8 in. glass column (10% SP 2330, 100/120 mesh Chromosorb W AW) and by 300-MHz FT-NMR. The alcohol **9** derived from the enantiomerically pure matrix showed specific rotation $[\alpha]_D^{25} -9.76$ (c 0.72, CCl_4).

Photolysis of diphenyldiazomethane in an Enantiomerically Pure Matrix at 137 K. Two 250- μL aliquots of a 0.1 M solution of diphenyldiazomethane in (S)-(+)-2-butanol were placed in two 5-mm Pyrex tubes containing 3-mm glass rods inside. The samples were sealed under vacuum after 3 freeze–pump–thaw cycles. Photolysis time was 128 min with thawing in the dark after 61 min.

After photolysis the samples were not allowed to decay overnight; they were thawed, the tubes opened, and the unreacted diazo compound quenched with acrylonitrile. A total of 4.1 mg (58% of theoretical) of **9** was isolated. Conditions for separation are shown below: eluent, 2.5% ethyl acetate/hexane; flow, 10 mL/min (pump = 3.5); collector, 130 s/sample; column size, A, LiChroprep (240–10) EM reagent; specific rotation is $[\alpha]_D^{25} -10.8$ (c = 0.25, CCl_4).

Variable-Temperature Photolyses and Product Studies. Solutions of diphenyldiazomethane (0.1 M, 250 μL) in D,L -2-butanol with naphthalene as an internal standard were placed in 5-mm Pyrex tubes equipped with 3-mm glass rods. Both had been thoroughly washed with ammonium hydroxide and oven-dried overnight before use.

The samples were sealed under vacuum after 3 freeze–pump–thaw cycles and photolyzed with use of two Rayonet RPR 3500 (3500 Å) lamps. After photolysis all samples were rapidly placed in liquid nitrogen and allowed to stand at 77 K overnight. The tubes were thawed and opened and an excess of acrylonitrile was added to quench unreacted diazo compound.

The samples were analyzed immediately by gas chromatography with a Hewlett-Packard 5830A GC equipped with a 6 ft \times 1/8 in. column (stainless steel 10% sp 2330, 100/120 mesh Chromosorb W AW). Product assignments were again made on the basis of GC/MS and by comparison with the mass spectra of authentic samples and coinjection.

Materials. (S)-(+)-2-Butanol²⁰ and hydroxy acid **16**¹² were resolved by literature methods. Compounds **8**,²¹ methyl 2,2-diphenylcyclopropyl ketone,^{22,23} 5,5-diphenyl-2-pentanone,²⁴ **13**,²⁵ **17**,²⁷ and **18**²⁸ were prepared as described in the literature.

1,1-Diphenyl-2-methyl-2-butanol (9). A solution of benzhydryllithium (38 mL, 17 mmol, 0.46 N) was cooled to -78°C by means of a dry ice–acetone bath. Methyl ethyl ketone (4.3 g, 5.4 mL, 0.06 mol) was dissolved in 5 mL of anhydrous ether and syringed into the flask. After addition, the now clear orange mixture was allowed to stir at -78°C for 20 min and slowly brought to room temperature. Unreacted benzhydryllithium was quenched with H_2O , the organic layer was separated, dried over MgSO_4 , and filtered, and the solvent was evaporated affording 12 g of a yellow oil which showed two spots on TLC (10% ethyl acetate/hexane, $R_{f1} = 0.7$, $R_{f2} = 0.3$ for desired alcohol).

Only 2 g of this oil was taken and purified by flash column chromatography with 7% ethyl acetate/hexane, until fraction 20, and then the polarity was increased to 10% ethyl acetate/hexane. Fractions 10 through 22 were mixed ($R_f = 0.35$) and the solvent evaporated, affording 1 g (0.004 mmol) of the desired tertiary alcohol. Alternatively an aliquot of the mixture was distilled at reduced pressure. Fractions 3 and 4 showed bp 121–123 $^\circ\text{C}/0.15$ mmHg; NMR shows (CDCl_3/TMS , 300 MHz) δ 7.35 (m, 10 H), 3.83 (s, 1 H), 1.5 (s, 1 H), 1.4 (q, 2 H, 8 Hz), 1.1 (s, 3 H), 0.9 (t, 3 H, 8 Hz); IR shows O–H at 3580–3470; m/e 168 (100), 167 (45), 73 (64) cm^{-1} ; exact mass observed ($\text{M}^+ - \text{H}_2\text{O}$)

222.1444, calculated 222.1411, difference, 0.0033.

1,1-Diphenyl-3-pentanol (10). A 100-mL, three-necked, round-bottomed flask equipped with N_2 inlet and outlet, condenser, septum, and spin bar was charged with 35 mL (0.0946 N solution in ether/hexane, 0.016 equiv) of benzhydryllithium. The red solution was cooled to -78°C by means of a dry ice–acetone bath. The 1,2-epoxybutane (Aldrich, 3.05 g, 3.65 mL, 0.040 mol) was syringed in 10 mL of ether solution while stirring. The solution was left stirring at -78°C for approximately 20 min then was brought slowly to room temperature and allowed to stir for an additional 30 min, followed by addition of H_2O . The organic layer was separated, dried over MgSO_4 , and filtered; the ether evaporated (30 $^\circ\text{C}/30$ mmHg) to afford a yellow viscous oil which showed three spots on TLC (20% ethyl acetate/hexane). The R_f of the major spot was 0.37; it was purified by flash column chromatography (12% ethyl acetate/hexane, Kieselgel 60, 230–400 mesh ASTM, EM Reagents) affording 1.6 g (0.007 mol, 42% yield) of the secondary alcohol **10**: NMR (CDCl_3/TMS , 300 MHz) shows δ 7.3 (m, 10 H), 4.2 (m, 1 H), 3.4 (m, 1 H), 2.2 (m, 2 H), 1.5 (m, 3 H), 1.18 (t, 3 H, 7.5 Hz); m/e 222 (45), 167 (100), 105 (40), exact mass observed 240.1512, calculated 240.1520, difference 0.0008; IR shows O–H at 3600–3450 cm^{-1} .

2-Butanol-2-d.²⁶ Into a 500-mL, three-necked, round-bottomed flask equipped with condenser, pressure-equalizing dropping funnel, spin bar, and N_2 inlet was placed LiAlD_4 (MSD 99 atom % D, 3 g, 0.06 mol) suspended in 40 mL of freshly distilled ether (over Na–benzophenone). Methyl ethyl ketone (4 g, 5 mL, 0.056 mol) was dissolved in ether (1:1 solution) and added slowly so that the reflux rate was mild. The reaction was left stirring overnight. A small amount of water (20 mL) was added until a white granular precipitate formed. The solution was filtered, the organic layer was separated, dried over MgSO_4 and filtered, and the solvent was evaporated. The liquid was distilled at atmospheric pressure, and only the middle fraction kept, affording 1.8 g, bp $98^\circ\text{C}/760$ mmHg; NMR (CDCl_3/TMS , 60 MHz) shows δ 2.0 (s, 1 H), 1.5 (q, 2 H), 1.3 (s, 3 H), 0.8 (t, 3 H). By MS % D incorporation is greater than 99%.

3-Methyl-4,4-diphenyl-2-butanol 11 and 12. A solution of benzhydryllithium in ether/hexane (39 mL, 0.46 N, 17.48 mmol) was syringed into a 100 mL, three-necked, round-bottomed flask equipped with gas inlet adapter, septum, and spin bar. The solution was cooled to -78°C by means of a dry ice–acetone bath. To it was added dropwise, with stirring, 3.65 mL (0.41 mol, 2.95 g) of either *cis*- or *trans*-2,3-dimethylloxirane by means of a syringe. After half the volume was added, the previously viscous solution stirred more freely and was followed by decolorization to pale yellow. When addition was complete, the mixture was allowed to stir 5–10 min at -78°C before allowing it to come to room temperature and was then left stirring for 30 min. The solution was quenched with water (25 mL) and left stirring for an additional 20 min. The ether layer was separated and washed with water (2×25 mL). It was dried over MgSO_4 and filtered and the solvent was evaporated, affording oils which were subsequently distilled under reduced pressure. Distillation did not prove useful so further purification was done by preparatory GC (GOW-MAC 550, 6 ft \times 1/4 in. 10% SE-30, 80/100 mesh Chromosorb W-AW). NMR (CDCl_3/TMS , 300 MHz): for **11**— δ 7.3 (m, 10 H), 3.8 (d, 1 H, 11 Hz), 3.7 (m, 1 H), 2.65 (m, 1 H), 1.5 (s, 1 H), 1.16 (d, 3 H, 6.9 Hz), 0.85 (d, 3 H, 7.2 Hz); for **12**— δ 7.3 (m, 10 H), 3.6 (d, 1 H, 11 Hz), 3.7 (m, 1 H), 2.65 (m, 1 H), 1.5 (s, 1 H), 1.10 (d, 3 H, 6.3 Hz), 0.82 (d, 3 H, 6.7 Hz); m/e 222 (20), 167 (100), exact mass observed 240.1497, calculated 240.1520, difference 0.0023 for **11** and observed 240.1510, calculated 240.1520, difference 0.0010 for **12**.

(R)-(+)-1,1-Diphenyl-2-methyl-2-butanol (9)²⁸. In a 25 mL three-necked, round-bottomed flask equipped with dry ice condenser, N_2 and NH_3 inlet, spin bar, and stopper were condensed 5 mL of ammonia at -78°C . To it was added a solution of *R*-(+)-**18** (0.4 g, 1.6 mmol) in 0.2 mL of ethanol and 0.4 mL of anhydrous ether. Sodium metal (50 mg, 2.2 mmol) was added gradually, in very small pieces during a 50-min period. The reaction mixture was then quenched by addition of a small amount of H_2O (1 mL), and the NH_3 was allowed to evaporate at room temperature. The ether layer was separated, dried over MgSO_4 , and filtered, and the solvent was evaporated affording an oil. This oil showed two spots on TLC ($R_{f1} = 0.35$, $R_{f2} = 0.22$, 10% EtOAc). The first component was isolated by means of flash chromatography (5% EtOAc), yielding 140 mg (0.58 mmol, 36% yield) of a clear film. The second spot was found to be starting material. The specific rotation $[\alpha]_D^{25}$ is +15.7 (c 7, CCl_4); m/e 168 (100), 167 (45), 73 (64), exact mass ($\text{M}^+ - \text{H}_2\text{O}$) observed 222.1432, calculated 222.1411, difference 0.0021.

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