Base-catalysed Ring Opening of 1,2-Diphenylcyclobutanols

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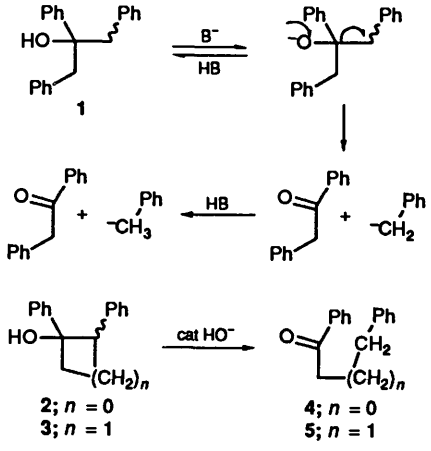
Cis- and *trans*-1,2-diphenylcyclobutanol have been prepared by literature methods and structural assignment confirmed by an X-ray crystal structure determination of the *cis* isomer. In the crystal structure, the four-membered ring has a pucker angle of 29° and the hydroxy group is pseudo-equatorial with respect to the puckered ring. In aqueous base, both isomers rearrange to 1,4-diphenylbutan-1-one. Rates of this reaction in buffered aqueous dioxane have been measured. The isomers are almost equally reactive, k_{cis}/k_{trans} *ca.* 0.7 at 25 °C, although empirical force field calculations suggest that the *cis* isomer is more strained by 3.5 kcal mol^{-1}. The solvent isotope effect, $k_{H,O}/k_{D,O}$, is 0.68, and discrimination isotope effect (k_H/k_D) in protonation of the benzylic site of the product is 0.99 ± 0.05. These ring openings are compared with those of the related cyclopropanols and with the corresponding reaction in a close acyclic analogue.

The paraffins in their all-staggered conformations are usually taken as unstrained molecules, and analysis of their heats of formation yields a measure of the contribution of a (CH_2) group to the heat of formation of a 'strainless' model of any other molecule.[1] Heats of formation of 'strainless' cyclopropane and cyclobutane obtained thus are −15.45 and −20.60 kcal mol^{-1} respectively, which compare with experimental heats of formation[2] of 12.73 and 6.78 kcal mol^{-1}.‡ These small rings may be regarded as strained by 28.3 and 27.4 kcal mol^{-1} respectively, and classically, the excess energy is associated with distortions from ideal values of bond angles and lengths, and with torsional or non-bonded interactions in the structures. Enhanced reactivity of small ring compounds in reactions in which the ring is cleaved and strain is relieved is to be expected and is well documented. What is less well understood is the large difference in reactivity of cyclopropanes and cyclobutanes despite the close similarity in their strains from thermochemical comparisons.[3] Cyclopropane derivatives are usually > 10^5 more reactive than their cyclobutyl homologues, but there are remarkably few direct comparisons available. Bury *et al.*[3] have examined reactivities of cyclopropanols and cyclobutanols in base-induced ring openings, thought to occur by anionic cleavage of the ring with subsequent or concerted protonation of the carbanionic group leaving from the alkoxide carbon. For the parent cycloalkanols, the ratio of second-order rate constants for the three- and four-membered rings is 1.6 × 10^8, and this ratio seems remarkably insensitive to substitution at either the 1- or 2-positions of the rings. Thus, while the rates for openings of cyclopropanol, 1-phenylcyclopropanol and 1-phenyl-2-phenylthiocyclopropanol are in the ratio of 1:7:700, reflecting stabilization at the carbanionic leaving group, the cyclopropyl:cyclobutyl ratio with the 1-phenyl and 1-phenyl-2-thiophenyl series are 1.3 × 10^9 and 1.5 × 10^8 respectively, so that the factor is less than 10 across the series.

We have recently examined decompositions of the alkoxide of 1,2,3-triphenylpropan-2-ol, **1**. Rate and product data for the reaction in DMSO solution are consistent with a rate-limiting collapse of the alkoxide by expulsion of benzyl anion followed by proton transfers to yield toluene and 1,2-diphenylethanone[4] as shown in Scheme 1. An interest in the relationships between structure and reactivity in these carbanion-forming reactions has led us to examine the reactions of the small ring 1,2-diphenylcycloalkanols, **2** and **3**, where the analogous reaction would yield **4** and **5**, also by collapse of alkoxide with expulsion of a benzylic anion. The base-catalysed reactions of *trans*- and *cis*-1,2-diphenylcyclopropanol, *t*-**2** and *c*-**2**, have already been examined by Jencks and Thibblin,[5] but not the corresponding cyclobutanols. We now describe and compare the reactions of their homologues, the cyclobutanols *t*-**3** and *c*-**3**.



Scheme 1 Anionic cleavage of tertiary alcohols

Results and Discussion

Preparation and Structures.—The isomeric cyclobutanols were first reported by La Count and Griffin[6] as products of sensitized irradiation of 1,4-diphenylbutan-1-one, then more recently as products of hydration[7] of 1,2-diphenylcyclobutene. We adopted the photochemical procedure of La Count and Griffin and obtained a mixture of the *cis*- and *trans*-1,2-diphenylcyclobutanols (*ca.* 15%) with acetophenone and styrene arising from Norrish type II cleavage.

The less polar of the alcohols was isolated as a colourless oil. The more polar was crystalline, showing properties in agreement with those reported by La Count and Griffin for the *cis* isomer. Their assignment of isomers was based on observation of the O*H* signals at δ 3.52 in the ^{1}H NMR spectrum of the crystalline isomer and at δ 1.75 in the other, with the difference

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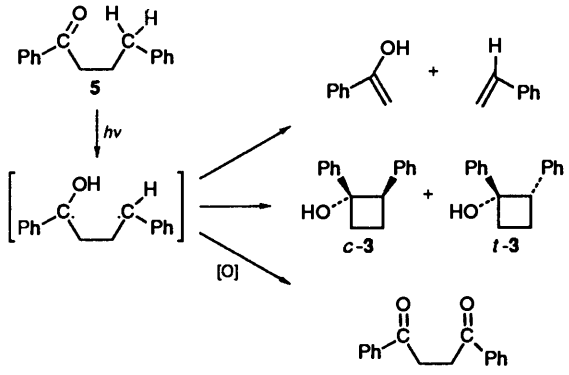
‡ 1 cal = 4.184 J.



Scheme 2 Preparation of *cis*- and *trans*-1,2-diphenylcyclobutanols

Table 1 ^{1}H NMR spectrum of crystalline isomer

		Coupling (Hz) to				
δ	Assignment	*H*-2	*H*-4a/b	*H*-4a/b	*H*-3a/b	*H*-3a/b
3.9	H-3		0.50	0.00	5.00	5.00
2.82	H-4a/b	0.50		5.50	0.50	4.80
2.38	H-4a/b	0.00	5.50		5.50	5.80
2.18	H-3a/b	5.00	0.50	5.50		6.10
2.01	H-3a/b	5.00	4.80	5.80	6.10	

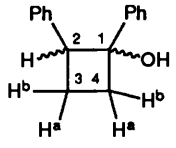


Fig. 1 Labelling of atoms in 1,2-diphenylcyclobutanols

between the two plausibly attributed to shielding of OH by the adjacent 2-phenyl group in the *trans* isomer. Since vicinal coupling constants in cyclobutanes have yielded stereochemical information in favourable cases,[8] we sought supporting evidence for this assignment in the high field ^{1}H NMR spectra of the isomers. At 300 MHz, all the signals from the cyclobutane ring of the crystalline isomer were resolved and decoupling experiments established the coupling patterns as shown in Table 1. Unfortunately, the couplings from H-2 to the adjacent methylene (H-3a/b) are equal. Other vicinal couplings are also similar so that the pattern did not establish stereochemistry. Overhauser effects were determined and were not useful. For the non-crystalline isomer, signals were not well resolved, with signals from the methylenes, H-3a, b and H-4a, b, appearing as overlapping multiplets. The signal from H-2 was resolved as a triplet at δ 4.05, again with near equal couplings to the adjacent H-3a, b methylene.

The assignment of isomers was finally secured by an X-ray crystal structure determination of the crystalline isomer which turned out to be the *cis* isomer in agreement with the original assignment of La Count and Griffin. The crystals contain a racemate and the molecular structure of the two molecules of *cis*-1,2-diphenylcyclobutanol that form the asymmetric unit in this triclinic crystal structure are depicted in Fig. 2. The postscripts A and B have been used to identify each molecule. Positional parameters, bond lengths and angles, torsion angles involving the non-hydrogen atoms, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

* For details of the deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

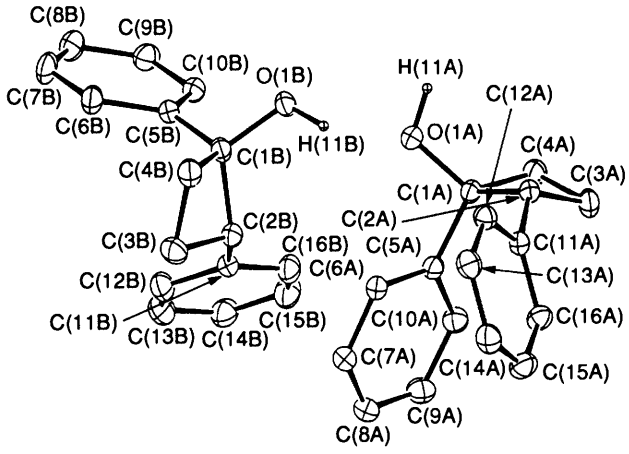


Fig. 2 An ORTEP plot of the two molecules of *cis*-1,2-diphenylcyclobutanol which make up the asymmetric unit. Ellipsoids are drawn at the 20% probability level and all hydrogens bonded to carbon have been omitted for clarity. A hydrogen-bond is formed by O(1B)–H(11B)···O(1A).

Molecules A and B associate such that a hydrogen bonding interaction, of length 2.801(3) Å, is formed between the O(1B) and O(1A) atoms. The crystal lattice is stabilized by hydrogen bonding interactions to an adjoining asymmetric unit which in effect locks four molecules together. This is formed between O(1A) and O(1B), 2.771(2) Å, with the latter atom related by the symmetry operation $-x, -y + 1, -z$. Such an interaction would not be possible with the *trans* isomer and may go some way to explaining why only crystals of the *cis* form have been obtained. The four-membered rings are puckered[9] by approximately 29° with phenyl substituents occupying one each of the axial and equatorial positions on the four-membered ring. The hydroxy groups are in equatorial positions.

Molecular mechanics[10] calculations of the isomeric cyclobutanols revealed local energy minima corresponding to two different puckered conformations of the cyclobutane rings. For the *trans* isomer, the lowest energy conformation has phenyl groups equatorial with respect to the ring. The conformation with both phenyls axial is 5.3 kcal mol^{-1} higher in energy, and this conformation will not be significantly populated at room temperature. For the *cis* isomer, both conformations must have one equatorial and one axial phenyl, and differ in the arrangement of the hydroxy group. The energy difference between conformations with equatorial and axial hydroxy groups is only 0.46 kcal mol^{-1}, and both will be populated at room temperature. Interestingly, the calculations, which relate to isolated molecules in the gas phase, show that the one with an equatorial hydroxy group found in the crystal structure is the higher energy of the two, and favourable hydrogen bonding and crystal packing forces probably account for the preference in the solid. The general features of the calculated and experimental structures are in good agreement, but the calculated structure is more puckered with a pucker angle of 38° as opposed to 29°. The relative energies of the isomeric cyclobutanes and their conformations is shown in Fig. 3, and are a measure of the relative amounts of strain in these molecules.

Rate and Product Studies.—Preliminary experiments showed that treatment of either isomer base in aqueous dioxane cleanly yielded the expected 1,4-diphenylbutan-1-one. No equilibration of the isomers was observed, nor was any elimination of water yielding 1,2-diphenylcyclobutane. When the reaction is run in D_2O, the product incorporates one deuteron at the 4-position, and varying amounts of deuterium at the enolizable 2-position. Reactions were conveniently monitored by sampling and HPLC analysis at intervals. Disappearances of the alcohols

Table 2 Rate data for base-induced ring openings of 1,2-diphenylcyclobutanols

Compound	Solvent[a]	T/°C	k_{obs}/s^{-1}	Parameters[b]
cis-**3**	H_2O–Dioxane	89.1	2.18×10^{-4}	
	H_2O–Dioxane	79.3	6.13×10^{-5}	
	D_2O–Dioxane	79.3	8.93×10^{-5}	$k_{H_2O}/k_{D_2O} = 0.69$
	H_2O–Dioxane	69.5	1.33×10^{-5}	
	H_2O–Dioxane at pH 11.62	25.0	5.8×10^{-9}[a]	$\log k = 17.61(\pm 0.81) - 7.70(\pm 0.29) \times 10^3/T$
trans-**3**	H_2O–Dioxane	89.1	2.00×10^{-4}	
	H_2O–Dioxane	79.3	5.90×10^{-5}	
	D_2O–Dioxane	79.3	8.73×10^{-5}	$k_{H_2O}/k_{D_2O} = 0.68$
	H_2O–Dioxane	69.5	1.35×10^{-5}	
	H_2O–Dioxane at pH 11.62	25.0	7.9×10^{-9}[c]	$\log k = 16.80(\pm 0.81) - 7.42(\pm 0.29) \times 10^3/T$

[a] pH measured at 25 °C. [b] Arrhenius plots $R^2 = 0.999$ for both isomers. [c] Extrapolated from higher temperatures.

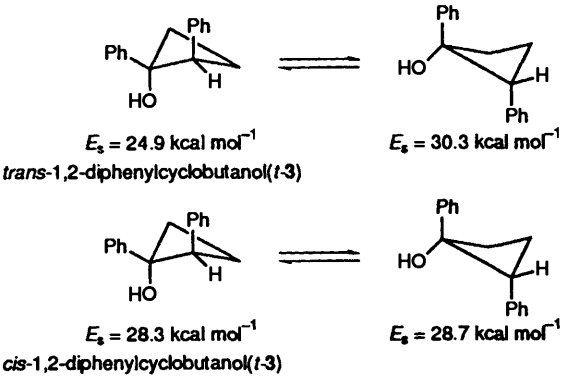


Fig. 3 Conformations and steric energies of *cis*- and *trans*-1,2-diphenylcyclobutanols

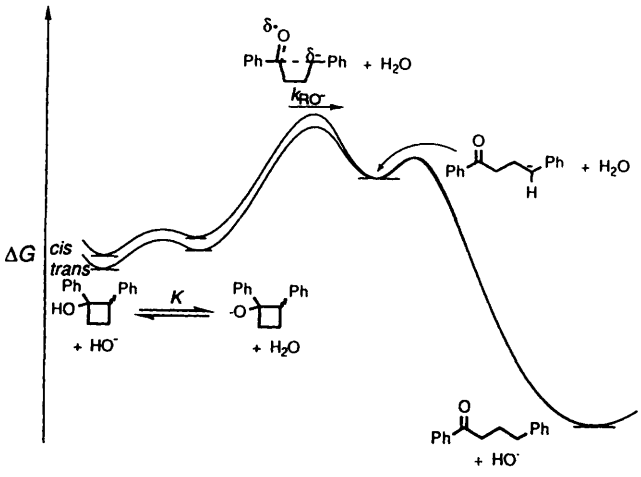


Fig. 4 Energy profile and reaction scheme

were accurately first order, and rates were determined using mixtures of the alcohols in solutions buffered with phosphate at pH 11.6. The collected rate data are presented in Table 2.

The kinetic solvent deuterium isotope effect, $k_{H_2O}/k_{D_2O} = 0.68$, is inverse, and close to that expected for the equilibrium secondary isotope effect[11] for ionization of heavy and light water. Any superimposed primary effect must be small, and the observation does not support concerted proton transfer in the transition state for the cleavage of these compounds. An isotope discrimination effect for incorporation of proton at the benzylic carbon of the 1,4-diphenylbutanone was also determined by measuring deuterium incorporation in the product in H_2O/D_2O mixed solvent. The effect is small ($k_H/k_D = 0.99 \pm 0.05$), and comparable with that for hydrolyses of the benzyl anion–sodium ion pair which occurs at near diffusion controlled rates[12] in aqueous THF. Taken together, the solvent and discrimination isotope effects support a reaction scheme for the cleavage in which the alkoxide reacts in the rate-determining step to yield a benzylic anion which then reacts with water in a discrete second step to yield product. The relevant relationships are:

$$v = k_{obs}[ROH]$$

where

$$k_{obs} = k_2[HO^-]$$

and

$$k_2 = k_{RO^-}K/[H_2O]$$

where k_{RO^-} and are defined as shown in Fig. 4.

The relative energies in this figure follow from the free energies of formation of *trans*-1,2-diphenylcyclobutanol, *t*-**3**, and the product ketone, **5**, calculated from Bensons[13] group energies (−29.3 and −51.9 kcal mol^{-1} respectively) and an assumption that the acid–base properties of the benzylic site in the ketone are those of a simple alkyl substituted toluene (pK_a *ca.* 42[14]) so that the carbanionic intermediate in aqueous medium is expected to lie 36.0 kcal mol^{-1} above the ketone product and thus 13.4 kcal mol^{-1} above the cyclobutanols. At 25 °C, the second-order rate constants for the ring opening, k_2, are 1.4×10^{-6} dm^3 mol^{-1} s^{-1} (*cis*) and 1.9×10^{-6} dm^3 mol^{-1} s^{-1} (*trans*) giving a free energy of activation $\Delta G^{\ddagger}$ *ca.* 25.4 kcal mol^{-1}. The observation that isomers are almost equally reactive (k_{cis}/k_{trans} *ca.* 0.7 at 25 °C) despite the difference in their calculated ground state strains (3.4 kcal mol^{-1}) suggests that the ground state strain is not completely released in the diastereomeric transition states leading to the intermediate carbanions, which would be formed initially in gauche-butane conformations rather than the depicted extended array.

There is no evidence that cyclobutanols are more acidic than their acyclic analogues, and if the acidity of the cyclobutanols is taken to be the same as 2-phenyl-2-propanol ($pK_a = 16.1$)[15] an approximate value for the rate constant for decomposition of the alkoxide, k_{RO^-} *ca.* 2×10^5 s^{-1} at 25 °C, can be obtained. We have not been able to observe cleavages of acyclic analogues in aqueous medium. For example 1,2,3-triphenylpropanol, **1**, is recovered unchanged after 10 days in 0.25 mol dm^{-3} NaOH in aqueous dioxane at 90 °C. For the cleavage of 1,2,3-triphenylpropanol, **1**, in DMSO solution the corresponding rate constant for decomposition of its alkoxide was measured directly ($k_{RO^-} = 8.5 \times 10^{-3}$ s^{-1} at 18.6 °C)[4] yielding a rate ratio of *ca.* 10^7 which must be regarded as a minimum estimate

for the rate enhancement associated with release of ring strain in the cyclobutoxide, since it masks an unquantifiable, but probably large, contribution from preferential solvation of the cyclobutoxide by water.

As noted earlier, Jencks and Thibblin[5] found that *cis*- and *trans*-1,2-diphenylcyclopropanol, *c*-**2** and *t*-**2**, suffered analogous ring opening yielding 1,3-diphenylpropan-1-one, **4**. At 25 °C, at pH 8.1, in aqueous acetonitrile observed rate constants for the isomers were 4.9 and 1.8×10^{-4} s^{-1} respectively. These ring openings showed only weak general acid catalysis ($\alpha \leqslant 0.1$) and a similar solvent isotope effect ($k_{H_2O}/k_{D_2O} = 0.7$). Unfortunately, a solvent discrimination effect was not determined, but the available data suggest that the mechanisms of ring openings of these particular cyclopropanols and cyclobutanols are similar and values for k_2, 3.9×10^2 (*cis*) and 1.4×10^2 (*trans*), may be obtained for the cyclopropanols. The 1,2-diphenylcyclopropanols are thus *ca.* 10^8 more reactive than their homologues in aqueous base, so that the constancy of the cyclopropanol/cyclobutanol ratio which we noted earlier is maintained, despite the fact that 1,2-diphenyl-substituted cycloalkanols are now 10^7 more reactive than the parent cycloalkanols. This ratio reflects both the effect of differences in acidity of the alcohols and reactivity of the alkoxides. Cyclopropanols, however, are more acidic than acyclic analogues with the 1-phenylcyclopropanol having $pK_a = 14.1$.[5] The reactivity ratio of the cyclopropoxides and cyclobutoxides (k_{RO^-}) is therefore 10^6.

Experimental

GLC was carried out on a Carlo Erba 4130 chromatograph fitted with a capillary column (5 m × 0.22 mm) with an 0.25μ OV-1 cross-bonded stationary phase, and hydrogen at 1 cm^3 min^{-1} as carrier gas. Merck precoated silica plates (0.25 mm Kieselgel 60 F_{254}) were used for analytical TLC and 20 × 20 cm plates coated with Merck Kieselgel 60 PF_{254} at 20 g per plate for preparative TLC. Kieselgel H and a range of solvents, all distilled before use, were used in column chromatography. IR spectra were recorded on a Perkin-Elmer 1710-FT spectrometer, routinely on thin films on NaCl plates. UV spectra were recorded on a Shimadzu UV-260 spectrometer on solutions in 95% aqueous ethanol. Routine ^1H and ^{13}C NMR spectra were run on a Bruker AC 300E spectrometer operating at 300 and 75 MHz respectively. Chemical shifts are reported in ppm (δ) relative to internal TMS. *J* values are in Hz. Mass spectra were run on a Kratos Concept LS1, using electron impact ionization at 70 eV or chemical ionization with ammonia as the reagent gas. Melting points were determined on a Kofler hot stage microscope and are uncorrected.

Cis- *and* trans-1,2-*Diphenylcyclobutanols* (*method of La Count and Griffin*.—4-Phenylbutyrophenone (Janssen Chemical) (4.5 g) was dissolved in distilled acetone (100 cm^3) and placed in the well of a photochemical apparatus. The solution was deoxygenated by a stream of argon, which also served to stir the solution before irradiation at room temperature using a 450 W Hanovia mercury lamp fitted with a quartz filter. The course of reaction was monitored by GLC analysis, and when all the butyrophenone was consumed, the solution was transferred to a round bottom flask, and solvent removed under water pump vacuum. The residue was then distilled ($T < 50$ °C, at 0.5 mmHg) in a bulb-to-bulb apparatus to remove styrene and acetophenone. Distillation was continued until the IR carbonyl band of the acetophenone was absent in the spectrum of the distillation flask residue which was then a viscous yellow oil (0.81 g). GLC showed the presence of three major components, ratio 1:0.81:0.15. Preparative thin layer chromatography on silica, eluting with 50:50 diethyl ether:petroleum, yielded pure samples of each of these. The minor component, shown by chromatographic and spectrographic comparison with an authentic sample to be 1,4-diphenylbutane-1,4-dione, crystallized as needles, m.p. 145–147 °C (lit.,[16] 145 °C). The faster moving major component was isolated as a colourless oil (*trans*); ν_{max}/cm^{-1} 3548, 3442, 3026, 2946, 1601, 1495, 1287, 1125 and 904; δ_H 1.97 (1 H, s, exchangeable with D_2O), 2.31 (2 H, m), 2.65 (2 H, m), 4.05 (1 H, t, *J* 5.3), 7.2–7.6 (10 H, m); *m/z* (CI) 223 (2.4), 207 (100), 120 (14), 105 (19) and 78 (12). The second component was isolated as a crystalline solid m.p. 88–90 °C (lit., 89–90 °C); ν_{max}/cm^{-1} 3400, 3060, 2981, 1601, 1496, 1448, 1228, 1128 and 1073; δ_H see text; *m/z* (CI) 223 (17), 207 (100), 120 (16), 105 (16), 78 (13) and 69 (35).

Kinetic and Product Studies.—Buffers were made up by dissolving sodium phosphate (0.79 g) in 70:30 (wt:wt) water–dioxane (50 cm^3). For solvent isotope effects, dioxane and deuterium oxide were weighed to give a solvent mixture with the same molar ratio of components; sodium phosphate (0.158 g) was dissolved in a mixture of 7.7 g D_2O and 3.0 g dioxane. Solution pHs measured at 25 °C using an EIL 7055 meter with combination electrode gave readings of 11.62 (H_2O) and 12.01 (D_2O). The glass electrode gives correct readings[17] in dioxane–water mixtures. Temperatures were controlled to ±0.05 °C in a Haake water bath. In a typical run, the isomeric alcohols and dibenzyl ether (*ca.* 1.0 mg of each) were weighed into a jacketed reaction vessel. Temperature was maintained at the reaction temperature by circulating water from an Haake E3 water bath through the jacket. The solvent base mixture (5.0 cm^3) was separately allowed to equilibrate before adding to the alcohols in the reaction vessel. After shaking for 1 min to ensure solution, the vessel was tightly stoppered, and the course of the reactions monitored by periodic sampling and analysis with the first sample (0.10 cm^3) taken immediately after mixing. Each sample was immediately treated with glacial acetic acid (0.025 cm^3) before storing until analysis by reverse phase HPLC on a 10 cm × 8 mm novapack 4μ ODS column, eluting with 55:45 (vol:vol) acetonitrile–water with UV detection at 220 nm. Retention times were *cis*-1,2-diphenylcyclobutanol: 5.11 min; *trans*-1,2-diphenylcyclobutanol: 7.51 min; 1,4-diphenylbutyrophenone: 12.66 min; and dibenzylether (internal standard): 10.94 min. Comparison with an authentic sample[18] of 1,2-diphenylcyclobutene, retention time 13.80 min, showed that it was not produced in the decomposition of the cyclobutanols. Pseudo-first-order rate constants were extracted from the data by non-linear least squares fitting of an exponential decay to the data. Product structure was confirmed by comparison with authentic 1,4-diphenylbutanone, both on HPLC and by GC/MS.

For the discrimination in H_2O/D_2O mixtures, buffered dioxane–H_2O and dioxane–D_2O mixtures were taken (2.57 and 2.78 g, respectively) to give a mixture with 50:50 molar ratio of H:D. The cyclobutanols (*ca.* 5 mg) were added and the mixture heated at 80 °C for 48 h. After cooling the mixture was diluted with water (10 cm^3), and extracted with light petroleum. After drying over anhydrous Na_2SO_4 and evaporation, the 1,4-diphenylbutanone was isolated by preparative TLC on silica and examined by ^1H NMR spectroscopy. Signals from the $PhCOCH_2-$ (δ 2.99), $CH_2CH_2CH_2-$ (δ 2.11) and $-CH_2Ph$ (δ 2.72) groups were integrated four times and average values taken. The central methylene (signal at δ 2.11) was taken as reference for a non-exchanging site to measure deuterium incorporations. The ratio of XCH_2CH_2Ph to XCH_2CHDPh was 2.00 (±0.13). Correction for the initial deuterium content in the water gives a discrimination isotope effect of 0.99 (±0.05).

Crystal Data for cis-1,2-*Diphenylcyclobutanol*.—$C_{16}H_{16}O$, $M = 224.30$, triclinic, $a = 10.907(2)$, $b = 13.011(3)$, $c =$

9.360(1) Å, α = 95.00(5), β = 89.47(5), γ = 104.20(1)°, V = 1283.0(2) Å^3, space group $P\bar{1}$ (No. 2), Z = 4, D_c = 1.161 g cm^{-3}, μ(Cu-Kα) = 5.14 cm^{-1}, final R = 0.051, final Rw = 0.066.

X-Ray Structure Determination of cis-1,2-*Diphenylcyclobutanol*.—Large, pale straw coloured prisms were obtained by slow evaporation of dichloromethane solvent at ambient temperature. One such crystal of dimensions 1.00 × 1.00 × 0.30 mm was mounted on a glass fibre with an epoxy resin for subsequent diffraction experiments using a Rigaku AFC5 diffractometer. X-Rays were provided by a Rigaku RU2000 rotating anode operating with settings of 50 kV, 100 mA, graphite monochromated (λ = 1.5418 Å), 1.0 mm incident collimator, 400 mm crystal to detector distance utilizing a continuously evacuated beam tunnel to reduce absorption by air. Unit cell constants and orientation matrix were determined from a least-squares refinement of the setting angles for 22 reflections (56.25 < 2θ < 64.56°). Data were measured at 295 K with $\omega/2\theta$ scans to a maximum 2θ of 120°; scan speed 16.0° min^{-1} with reflections having $I < 10.0\sigma$ scanned in triplicate to improve counting statistics, scan width (1.31 + 0.30 tan θ)°. 3179 measurements (including three standards measured repetitively throughout the experiment), 3002 unique of which 2625 with $I > 3.0\sigma(I)$ were considered observed. A decay factor, according to the behaviour of the standards, of 4.2% was applied. Data were corrected for Lorentz-polarization effects and absorption[19] (minimum transmission of 0.77). The structure was solved by direct methods.[20] Hydrogen atoms were placed in calculated positions or located in difference Fouriers. The refinement was by full-matrix least-squares minimization of $w(F_o - F_c)^2$, with $w = 4F_o^2/\sigma^2(F_o)^2$. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were assigned isotropic thermal parameters 20% greater than the equivalent B value of the atom to which they were bonded. The observations/variables ratio is 6.03, the maximum shift/error in the final cycle of least-squares is 0.09 and the maximum and minimum peaks in the final difference Fourier synthesis are 0.19 and −0.13 e$^-$ Å^3 respectively. Atomic scattering factors were calculated according to Cromer and Waber.[21] Anomalous dispersion effects were included in F_c.[22] All calculations were carried out on a VAX station 3520 with the TEXSAN package.[23] Fig. 2 was obtained with ORTEP.[24]

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