disturbances in the structure of the micelle-bonded water, a process which will lead to an increase in the disorder of the system. Although the contribution of this factor is difficult to quantify, its importance is likely to be higher in the case of a nonionic reversed micelle than for an ionic one (e.g., AOT).

The observed decrease in the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as a function of increasing $R$ can be rationalized as follows. $^1$H NMR studies showed that the mobilities of the water molecules and of the surfactant oxyethylene groups increase as a function of increasing $R$, due to diminished surfactant–water interactions.[14] The variation of $\Delta H^{\ddagger}$ can be attributed to a decrease in the stabilization of the RS accompanied by an enhanced stabilization of the TS through solvation by the surrounding water molecules (these become more free to form hydrogen bonds as the size of the water pool is increased). Both factors are also responsible for the observed dependence of $\Delta S^{\ddagger}$ on $R$.

## Experimental Section

The drying of the solvent (Merck, Uvasol), the purification of DCA (Fluka), and proofs of its purity were given elsewhere.[5] TX-100 was purified by column chromatography,[16] and its purity was established as given before.[17] The surfactant was dried in vacuo for several days before making up the stock solution (1 M), which was renewed daily. Partially deuterated surfactant was prepared by dissolving $D_2O$ (Aldrich, 99.8% D) in a 1 M surfactant solution in $CCl_4$, followed by distilling off the solvent. This procedure was repeated twice. $^1$H NMR peak integration (Varian T-60) showed a 50% deuteration of the OH group.

The reaction was followed by monitoring the disappearance of the carbonyl group of DCA at 307 nm, with a Zeiss PM6KS spectrophotometer. The reaction was initiated by injecting 10 $\mu$L of a 0.75 M ketone solution in 0.4 mL of a 0.38 M surfactant solution containing the appropriate concentration of solubilized water or $D_2O$. Observed rate constants ($k_{obsd}$) were obtained from the absorbance–time data. The percent relative standard deviations (i.e., the standard deviation × 100/$k_{obsd}$) were < 3%. The constants $k_h$, $k_d$, and $K_h$ can be calculated from the initial absorbance ($A_0$) and that at equilibrium ($A_e$) with the following equations:[4,5]

$$K_h = (A_0 - A_e)/A_e$$

$$k_h = k_{obsd}\,(A_0 - A_e)/A_0$$

$$k_d = k_{obsd}\,(A_e/A_0)$$

**Acknowledgment.** We thank the FAPESP and CNPq Research Foundations for financial support.

**Registry No.** $D_2O$, 7789-20-0; DCA, 534-07-6; Triton X-100, 9002-93-1; aersol-OT, 577-11-7; $H_2O$, 7732-18-5; $(ClCH_2)_2C(OH)_2$, 82598-72-9.

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# Synthesis of 1,4-Cyclohexadienylbis(benzylidene)

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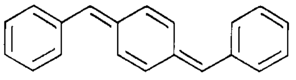
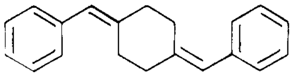
We report the synthesis of 3,6-dibenzylidene-1,4-cyclohexadiene (I), the model compound in our ongoing study of the synthesis and properties of conducting polymers.



I



II

We have pursued the following unsuccessful paths to I:

(a) Sulfuric acid catalyzed dehydration of *p*-benzylbenzohydrol (III). Only the corresponding ether, IV, resulted.

(b) Potassium *tert*-butoxide dehydrobromination of $\alpha,\alpha'$-diphenyl-$\alpha$-bromo-*p*-xylene (V).

(c) Wittig reaction[2] between benzyltriphenylphosphonium chloride and 1,4-cyclohexanedione in the presence of phenyllithium and ethyl ether as solvent to give 1,4-dibenzylidenecyclohexane (II) followed by NBS bromination of II followed by dehydrohalogenation in the presence of Zn and NaOH. The product could not be freed of bromine.

(d) Dehydrobromination of 1,4-bis($\alpha$-bromobenzyl)-1,4-dibromocyclohexane (VI) gave only 1,4-bis($\alpha$-bromobenzylidene)cyclohexane (VII).

Since II was easy to prepare, we explored the dehydrogenation of II as a possible route to I. We first selected chloranil,[3-5] as dehydrogenating agent. Although we could isolate and identify the reduction product, tetrachlorohydroquinone, we could not isolate the corresponding oxidation product I. Use of the stronger agent 2,3-dichloro-5,7-dicyanobenzoquinone[4-7] (DDQ) led to pure I.

Carrying out the Wittig reaction to product II in N,N-dimethylformamide (DMF) as solvent gave a 40% yield of a mixture of I and II. Reaction of this mixture with DDQ also gave pure I.

The $^1$H NMR spectra show benzylidine protons at 6.4 ppm in I and 6.2 ppm in II. Both compounds have virtually identical UV spectra. There were considerable differences in the infrared spectra of compounds I and II, however. The complexity of the $^1$H NMR spectra in the regions near 2 and 6 ppm suggests that both I and II were obtained as mixtures of cis–trans isomers.

## Experimental Section

**1,4-Dibenzylidenecyclohexane (II).** A solution of 0.1 mol of phenyllithium in 70/30 cyclohexane/ether was diluted to 150 mL with anhydrous ether under $N_2$. Benzyltriphenylphosphonium chloride (BTPC; 0.1 mol) was added. The ensuing reaction was exothermic and the mixture turned orange. After 1 h, 0.05 mol of 1,4-cyclohexanedione was added and the mixture heated under reflux for 4 days under $N_2$. Color gradually changed to a light tan. After cooling and filtering, the solution was washed with aqueous $NaHSO_3$ solution and then several times with water. The organic layer was dried over $MgSO_4$ and evaporated to turbidity. Addition of methanol yielded a white crystalline product, II, in 25% yield: mp 110–112 °C; IR (KRr pellet) 1600, 1665, 3010, 2880 cm$^{-1}$; $^1$H NMR ($CCl_4$) $\delta$ 2.4 (s, 8), 6.2 (s, 2), 7.1 (s, 10); UV (cyclohexane) 295 nm, 305, 320.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found C, 92.08; H, 7.90.

**Wittig Reaction in DMF.** The above reaction was repeated with the modification of diluting the phenyllithium solution with DMF instead of ether. The product, 33%, melted at 107–108 °C and was found to be a mixture of II and I by elemental, IR, and NMR analysis.

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J. Org. Chem. 1982, 47, 3987–3991

**Dehydrogenation of II.** To 0.0114 mol of II in 35 mL of benzene under $N_2$ was added slowly 0.25 mol of DDQ dissolved in 70 mL of benzene. After the mixture was refluxed for 30 h, the benzene was evaporated to dryness. The residue was extracted with ligroin, and this solution was passed through an alumina column, which removed a slight green color. Evaporation of the petroleum solvent yielded white crystals of compound I in 12% yield: mp 126–128 °C; IR (KRr pellet) 1600, 1665 $cm^{-1}$; $^1H$ NMR ($CCl_4$) $\delta$ 2.7 (m, 4), 6.4 (m, 2), 7.2 (s, 10); UV (cyclohexane) 295 nm, 305, 320.

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.79; H, 6.40.

**Preparation of *p*-Benzylbenzohydrol (III).** The general procedure of Wiselogle and Sonnenborn[8] for the synthesis of benzohydrol was modified: A mixture of 20 g (0.074 mol) of *p*-benzoyldiphenylmethane,[9] 20 g (0.5 mol) of technical sodium hydroxide pellets, and 20 g (0.305 mol) of zinc dust in 200 mL of 95% alcohol was stirred. The mixture spontaneously warmed to about 65 °C. After 3 h, the cool mixture was suction filtered and the residue washed with alcohol. The filtrate was poured into 5 volumes of ice water acidified with 44 mL of concentrated HCl. A white cloudiness indicated the separation of the product. Filtration and drying under vacuum at 40 °C gave 19.5 g (98% yield) of III: mp 62–65 °C; IR (KBr pellet) 3300; $^1H$ NMR ($CCl_4$) $\delta$ 2.9 (s, 1), 3.8 (s, 2), 5.5 (s, 1), 7.2 (m, 14).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.55; H, 6.61. Found: C, 87.71; H, 6.71.

**Preparation of Bis[α-(*p*-benzylphenyl)benzyl] Ether (IV).** Attempts to synthesize I led instead to the ether bis[α-(*p*-benzylphenyl)benzyl] ether (IV). A mixture of 0.7 g (2.5 mol) of *p*-benzylbenzohydrol and 50 mL of a 10% solution of $H_2SO_4$ in water was stirred under reflux for 48 h. The lump of hard white solid that formed was filtered from the acid. The lump was powdered with a glass rod and washed with water and methanol to yield 0.645 g (95%). This ether is insoluble in $CS_2$, ethanol, DMS, very slightly soluble in boiling $CCl_4$, and soluble in hot benzene and hexachloro-1,3-butadiene. This product was extracted in a Soxhlet extraction apparatus with benzene and recrystallized by cooling the benzene solution: mp 191–192 °C; IR (KBr pellet) shows no OH or C=C bands; $^1H$ NMR (hexachloro-1,3-butadiene) $\delta$ 3.9 (s, 4), 5.4 (s, 2), 7.1 (s, 28).

Anal. Calcd for $C_{40}H_{34}O$: C, 90.55; H, 6.45. Found: C, 89.85; H, 6.51.

**Preparation of α,α′-Diphenyl-α-bromo-*p*-xylene (V).** Two methods were followed to obtain this compound.

**Method 1. Monobromination of *p*-Dibenzylbenzene.** A solution of 2.58 g (0.10 mol) of *p*-dibenzylbenzene[10] in 25 mL of $CCl_4$ was heated to reflux in a water bath, and 1.60 g (0.10 mol) of $Br_2$, dissolved in 25 mL of $CCl_4$, was added over a period of 3 h under a UV lamp. The evolved HBr was collected in a water trap. The mixture was left refluxing for 12 h under the UV lamp, when the solution was clear yellow. The solution was cooled, washed with water, 5% NaOH, and finally water and then dried with $MgSO_4$ overnight and filtered, and the solvent was removed by distillation. The residue crystallized after 2 days to yield 1.71 g (53%) of white crystals, mp 60–62 °C.

**Method 2. Bromination of III.** Although the NMR spectrum of the product obtained by method I indicated that there was bromination and the relative areas of the peaks were in accordance with the given structure, proof of structure is not conclusive because a mixture of unbrominated, monobrominated, and dibrominated compounds would give a very similar or identical spectrum. To avoid this uncertainty the hydroxyl group of III was substituted with a bromine atom. An excess of 48% solution of HBr in water was added to 2.74 g (0.10 mol) of III and the mixture stirred at room temperature for 3 h. When the mixture was heated to reflux, two layers immediately appeared. After 1 h the mixture was cooled, and the oily layer was extracted with $CCl_4$, washed several times with water, sodium bicarbonate, and water again to eliminate any traces of acid. The $CCl_4$ solution was dried overnight with $MgSO_4$ and filtered, and the solvent was removed by distillation. The monobromo compound crystallized, giving a total yield of 2.96 g (92%). This product was recrystallized from petroleum ether, giving white crystals melting at 60–62 °C. Both $^1H$ NMR and IR spectra were identical with those obtained by method 1: $^1H$ NMR ($CCl_4$) $\delta$ 3.8 (s, 2), 6.1 (s, 1), 7.1 (m, 14).

Anal. Calcd for $C_{20}H_{17}Br$: C, 71.22; H, 5.08; Br, 23.70. Found: C, 71.15; H, 5.12; Br, 23.63.

**Attempted Reaction of V with Potassium *tert*-Butoxide.** In an attempt to obtain I by 1,6-dehydrohalogenation of V, 1.05 g (3.1 mmol) of this reagent was mixed with 1.10 g (9.8 mmol) of potassium *tert*-butoxide in 40 mL. The mixture was heated under reflux under nitrogen atmosphere for 30 min. At the end of this period dehydrohalogenation had not occurred as indicated by IR and $^1H$ NMR spectra.

**Preparation of 1,4-Bis(α-bromobenzyl)-1,4-dibromocyclohexane (VI).** To 0.585 g (2.25 mmol) of II dissolved in 5 mL of $CCl_4$ was added 45.8 mL (4.58 mmol) of a 0.1 M solution of $Br_2$ in $CCl_4$ until the color did not fade. The $CCl_4$ was evaporated almost totally and ethyl ether was added to precipitate the product. The solid was filtered, redissolved in chloroform, and reprecipitated with ethyl ether. The white crystals were dried for 24 h under vacuum at 60 °C: mp 195.5–197.5 °C; $^1H$ NMR ($CCl_4$, 80 °C) $\delta$ 2.3 (s, 8), 5.1 (s, 2), 7.2 (m, 10).

Anal. Calcd for $C_{20}H_{20}Br_4$: C, 41.42; H, 3.48; Br, 55.11. Found: C, 41.23; H, 3.41; Br, 55.31.

**Preparation of 1,4-Bis(α-bromobenzylidene)cyclohexane (VII).** To 0.245 g (0.42 mmol) of VI was added 5 mL of a 20% solution of KOH in 95% ethanol and the mixture was heated under reflux in a water bath for 2 h. VII was filtered from the alcoholic solution and washed with water and alcohol several times. It was purified by crystallization from ligroin and from chloroform to yield 0.16 g (90%;) of white crystals: mp 175–180 °C; IR (KBr pellet) 1660 $cm^{-1}$; $^1H$ NMR ($CCl_4$, 85 °C) $\delta$ 2.5 (s, 8), 7.3 (s, 10).

Anal. Calcd for $C_{20}H_{18}Br_2$: C, 57.44; H, 4.34; Br, 38.22. Found: C, 57.30; H, 4.29; Br, 38.38.

**Attempted Preparation of I.** A procedure similar to that used by Velluz[11] was followed. To a solution of 0.691 g (2.66 mmol) of II in 10 mL of $CCl_4$ was added 2.0 g (11.25 mmol) of commercial *N*-bromosuccinimide and the mixture was refluxed for 30 min under UV light. The succinimide formed was removed by filtration and the solvent evaporated. The residue was purified by column chromatography and found to be a mixture of VI and I. To increase the ratio of I to VI, we carried out the same experiment under the same conditions, using freshly purified NBS; however, the purification of NBS did not affect the distribution of products. The cream-colored product could not be purified to yield a pure product as evidenced by poor elemental analyses.

**Registry No.** I, 82639-38-1; II, 82639-39-2; III, 82639-40-5; IV, 82639-41-6; V, 82639-42-7; VI, 82639-43-8; VII, 82639-44-9; benzyltriphenylphosphonium chloride, 1100-88-5; 1,4-cyclohexanedione, 637-88-7; *p*-benzoyldiphenylmethane, 58280-04-9; *p*-dibenzylbenzene, 793-23-7.

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# Absolute Configuration Determinations of Chiral α-Substituted Benzylamines Using Liquid Crystal Induced Circular Dichroism

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## Introduction

Absolute configurations of chiral compounds are routinely assigned on the basis of the rotation sign of plane polarized light at 589 nm. While this method has been useful, it is out of line with modern analytical techniques from the viewpoint of sensitivity. Chemical structures can

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