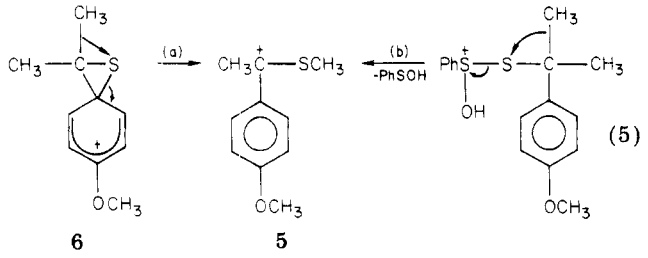

6 5 (5)

tonated thiosulfinate to replace the usual bimolecular path involving the alkyl sulfide, it is possible that the *p*-anisyl promotes the dissociation of protonated **1b** by stabilizing the positive charge that would develop on the carbon adjacent to the dicoordinate sulfur concomitant with migration of a methyl group, rather than by bridging, as in eq 2.

Experimental Section

1-Methyl-1-phenylethyl Benzenethiosulfinate (1a). Thionyl chloride (5.0 g, 0.042 mol) was slowly added with stirring to a solution of 2-phenyl-2-propanol (5.0 g, 0.037 mol) (Aldrich) in 10 mL of dry ether at 0 °C. After 2 h at room temperature, the solvent and excess thionyl chloride were removed under reduced pressure. The residue was added with stirring to thiourea (2.8 g, 0.037 mol) dissolved in the minimum amount of absolute ethanol, and the mixture was refluxed for 2 h. Sodium hydroxide (4.0 g), dissolved in a minimum amount of water, was added, and the solution was refluxed for an additional 2 h. The reaction mixture was poured into water and extracted with ether, the extracts were washed (H_2O) and dried ($MgSO_4$), and the ether was removed under reduced pressure. Distillation gave 4.6 g, bp 52–56 °C (1 mmHg), shown by ^1H NMR to be a mixture of 84% 2-phenyl-2-propanethiol [δ 1.8 (s, 6 H), 2.2 (s, 1 H), 7.4 (m, 5 H)] and 16% 2-phenyl-2-propanol [δ 1.51 (s, 6 H), 2.1 (br s, 1 H), 7.4 (m, 5 H)], the methyl singlets being used to determine the relative amounts of thiol and alcohol present. This mixture (4.6 g) of thiol and alcohol and pyridine (2.4 g) in 50 mL of anhydrous ether was added slowly at room temperature over 2 h to a stirred solution of freshly prepared benzenesulfinyl chloride[3] (4.8 g, 0.03 mol) in 50 mL of ether. The precipitate of pyridine hydrochloride was removed, the filtrate was washed (1 N sulfuric acid, 5% sodium bicarbonate, and water) and dried (Na_2SO_4), and the ether was removed. Thiosulfinate **1a**, mp 43–45 °C, was isolated (1.6 g, 20%) by crystallization from hexane at −78 °C: IR 1080 cm^{-1} (s, S=O); ^1H NMR ($CDCl_3$) δ 2.00 (s, 3 H) and 2.18 (s, 3 H), diastereotopic methyl groups in **1a**, 7.6 (m, 10 H, Ar H). Anal. Calcd for $C_{15}H_{16}O_2S$: C, 65.20; H, 5.85; S, 23.17. Found: C, 65.10; H, 6.06; S, 23.07.

1-(*p*-Anisyl)-1-methylethyl Benzenethiosulfinate (1b). *p*-Methoxyacetophenone (Aldrich) (10 g, 0.066 mol) was added to an equimolar amount of methylmagnesium iodide in ether, and the reaction mixture was worked up in the usual fashion, giving 8.0 g (73%) of crude 2-(*p*-anisyl)-2-propanol: NMR ($CDCl_3$) δ 1.51 (s, 6 H), 2.7 (br s, 1 H), 3.76 (s, 3 H), 7.15 (AA'BB' m, 4 H). Since attempted distillation of the crude alcohol gave olefin and tar, it was used without further purification.

To 3.0 g of 2-(*p*-anisyl)-2-propanol dissolved in 20 mL of glacial acetic acid was added 3 drops of concentrated sulfuric acid. The bright purple solution was warmed slightly and shielded from light, and hydrogen sulfide was passed through it for 45 min. The solution was poured into water and extracted with ether. The ether extracts were washed (5% sodium bicarbonate and water) and dried ($MgSO_4$), and the ether was removed under reduced pressure, yielding 2-(*p*-anisyl)-2-propanethiol (2.6 g, 79%): NMR ($CDCl_3$) δ 1.81 (s, 6 H), 2.2 (s, 1 H), 3.85 (s, 3 H), 6.8–7.7 (AA'BB' m, 4 H). Since the thiol loses H_2S and decomposes on attempted distillation, it was used without further purification. The infrared spectrum showed no alcohol was present as an impurity.

2-(*p*-Anisyl)-2-propanethiol (2.6 g) was reacted with benzenesulfinyl chloride (2.3 g) and the reaction mixture worked up in the same fashion as in the synthesis of **1a**. Low-temperature crystallization from hexane gave **1b** (0.60 g, 14%): mp 54–57 °C; NMR ($CDCl_3$) δ 1.97 (s, 3 H), 2.13 (s, 3 H), 3.81 (s, 3 H), 6.8–7.7 (m, 9 H); IR ($CHCl_3$) 3000, 1610, 1510, 1460, 1445, 1390, 1370, 1300, 1200 (s), 1080–1030 cm^{-1} (s, S=O). Anal. Calcd for $C_{16}H_{18}O_2S_2$: C, 62.73; H, 5.92. Found: C, 62.90; H, 6.05.

Kinetic Study of Decomposition of 1a and 1b. Solutions of **1a** and **1b** in acetic acid–1% H_2O alone show no change in UV absorption over a period of several days. Acetic acid–1% water (3.5 mL) containing the desired amounts of sulfuric acid and *n*-butyl sulfide was placed in a thermostated cell and 35 μL of a 0.01 M solution of either **1a** or **1b** in acetic acid–1% H_2O was added to follow the kinetics of the acid-catalyzed decompositions. The change in optical density with time at a suitable wavelength (268 nm for **1a**, 257 nm for **1b**) was then monitored. With **1b** the initial change in absorbance associated with the decomposition of **1b** was followed by a small further change in absorbance; this was slow enough and small enough, however, that there was no difficulty in determining the "infinity time" absorbance associated with the decomposition of **1b** itself.

Decomposition Products of 1b. Thiosulfinate **1b** (2.1 g, 6.9 mmol) was dissolved in 75 mL of acetic acid–1% water, sulfuric acid was added to make the solution 0.10 M in H_2SO_4, and the solution was allowed to stand at room temperature for 1 h. It was poured into water (225 mL) and extracted with ether. The ether extracts were washed (10% sodium carbonate and water) and dried ($MgSO_4$), and the ether was removed. The residue (2.0 g) was chromatographed on silica gel with successively hexane, carbon tetrachloride, and acetone (and mixtures of same) as eluants. The first fraction consisted of diphenyl disulfide (40 mg). This was followed by a minute amount (~20 mg) of 2-(*p*-methoxyphenyl)propene (**3**). A large amount of material (1.5 g) was eluted by 1:2 hexane–CCl_4 containing 5% acetone. One component of this material was shown to be *p*-methoxyacetophenone, identical in all respects with a known sample. The total amount of this ketone in the several fractions (0.40 g, 2.67 mmol) was estimated by NMR from the intensity of the δ 2.46 singlet for the $CH_3C(O)$ group. The remaining components of the mixture could not be satisfactorily separated and were not identified, although it was established from infrared and NMR examination that no significant amount of acetate **4** was present. The NMR also indicated that *p*-anisyl and phenyl groups were present in the different components in a ratio of 2:1.

Acknowledgment. Support of this research by the Robert A. Welch Foundation (Grant D-650) is gratefully acknowledged.

Registry No. **1a**, 73396-84-6; **1b**, 73396-85-7; 2-phenyl-2-propanol, 617-94-7; 2-phenyl-2-propanethiol, 16325-88-5; benzenesulfinyl chloride, 4972-29-6; *p*-methoxyacetophenone, 100-06-1; 2-(*p*-anisyl)-2-propanol, 7428-99-1; 2-(*p*-anisyl)-2-propanethiol, 73396-86-8.

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Evidence for a Hydroxyl Directing Effect in Dichlorocarbene Addition to 2-Cycloalkenols

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Received November 30, 1979

Introduction

The influence of hydroxyl groups on the stereochemical outcome of Simmons–Smith cyclopropanation[1] and epoxidation[2,3] of 2-cycloalkenols is well-documented. Complexation of the incoming reagent to the hydroxyl oxygen

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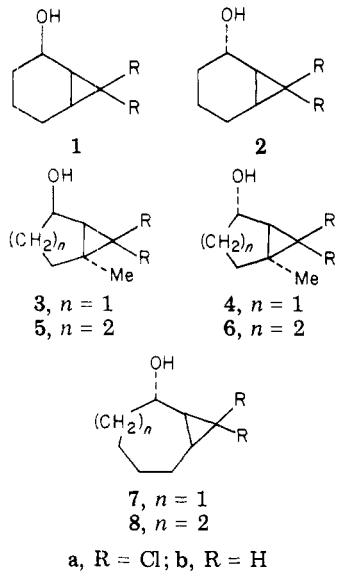
0022-3263/80/1945-2509$01.00/0

Chart I



1 2

3, n = 1
5, n = 2

4, n = 1
6, n = 2

7, n = 1
8, n = 2

a, R = Cl; b, R = H

directs attack at the proximate face of the olefin. With the more conformationally rigid five- and six-membered cycloalkenols, syn addition is observed. A crossover to anti addition usually occurs with medium-membered rings and results from conformations where the complexed reagent is closer to the anti face of the olefin.

Seyferth and co-workers[4] have reported that this hydroxyl directing effect was inoperative in dichlorocarbene addition to 2-cycloalkenols. They obtained only products of anti addition with 2-cycloheptenol and 2-cyclooctenol, using phenyl(bromodichloromethyl)mercury to generate dichlorocarbene. However, no simple adducts with 2-cyclohexenol were isolated due to competing reactions of dichlorocarbene with the alcohol group.

While examining the reaction of allylic alcohols with dichlorocarbene generated by phase-transfer catalysis (PTC), we observed that 2-cyclohexenol gave predominately (13:1) the syn adduct **1a** in 50% isolated yield. The stereochemistries of syn isomer **1a** and the minor anti isomer **2a** were established by reduction with lithium in ammonia[5] to give the known bicyclo[4.1.0]heptanols **1b** and **2b**[4] (Chart I). While this result seems inconsistent with those of Seyferth, further investigation confirmed the predominately syn addition of dichlorocarbene to five- and six-membered-ring allylic alcohols.

Although no simple adducts were isolated with 2-cyclopentenol as substrate, 3-methyl-2-cyclopentenol gave a mixture of syn adduct **3a** and anti adduct **4a** in a ratio of 2.3:1 in 85% yield. The adducts **5a** and **6a** were obtained in 72% isolated yield from 3-methyl-2-cyclohexenol in a syn:anti ratio of 15:1. With medium-membered rings, a dramatic change in the stereochemistry of addition was observed. Thus, 2-cycloheptenol and 2-cyclooctenol gave exclusively the anti adducts **7a** and **8a**, respectively. This parallels the results Seyferth[4] obtained. The stereochemistry of these adducts was ascertained by comparison with known spectral properties where available. In addition, **3a**, **5a**, **7a**, and **8a** were reduced to their known dihydro derivatives **3b**,[6] **5b**,[7] **7b**,[4] and **8b**.[4]

The crossover from syn to anti addition with medium-ring cycloalkenols has been associated with coordination of the reagent to pseudoequatorial alcohols.[3] Zn/CH_2I_2 and *m*-chloroperoxybenzoic acid exhibit this behavior and give 10% and 40%, respectively, of anti adducts with 2-cycloheptenol. The exclusive formation of anti alcohol **7a** with dichlorocarbene may result from differences in size and electronic character of the attacking species. These differences could influence the cycloheptene conformation[9] which 2-cycloheptenol adopts, giving rise to differing ratios of syn and anti adducts.

In conclusion, the pattern of stereoselective addition of dichlorocarbene to 2-cycloalkenols is strongly suggestive of a directing effect by the hydroxyl group.

Experimental Section

Melting points were determined with a Thomas-Hoover melting-point apparatus and are uncorrected. NMR spectra were determined on a Varian T-60 spectrometer. Gas-chromatographic analyses were carried out by using a Hewlett-Packard 5840A gas chromatograph equipped with a 10% OV-1 on 80–100 Chromosorb G column. Starting materials were either purchased from Aldrich or prepared according to literature procedures.[10-12]

General Procedure for Dichlorocarbene Addition. To a solution of 2-cycloalkenol (20 mmol) and benzyltrimethylammonium chloride (0.2 mmol) in 30 mL of $CHCl_3$ was slowly added 8 mL of 50% aqueous NaOH. The reaction mixture was stirred with cooling (water bath) for 2 h. Workup consisted of pouring the reaction mixture into 10% aqueous HCl followed by CH_2Cl_2 extraction. After the solution was dried over Na_2SO_4, concentration gave a crude product which was chromatographed on Florisil (ether–hexane as eluant). The dichlorocyclopropyl alcohols were obtained from the latter fractions and further purified by recrystallization where appropriate.

***endo*- and *exo*-7,7-Dichlorobicyclo[4.1.0]heptan-2-ols (1a and 2a).** Reaction of 2-cyclohexenol (84 mmol) with dichlorocarbene by the general procedure gave 7.2 g (47%) of adducts **1a** and **2a**. GC analysis of the mixture indicated this to be 93% endo alcohol **1a** and 7% exo alcohol **2a**. Chromatography of this mixture gave small amounts of exo alcohol **2b** as an oil (ca. 85% pure), NMR ($CDCl_3$) δ 3.70–4.00 (m CHOH). The latter fractions gave pure endo alcohol **1a** as a solid. Recrystallization from hexane gave material with mp 66–68 °C; NMR ($CDCl_3$) δ 3.94–4.44 (m, CHOH). Anal. Calcd for $C_7H_{10}Cl_2O$: C, 46.43; H, 5.57; Cl, 39.16. Found: C, 46.7; H, 5.4; Cl, 38.8.

Reduction of endo alcohol **1a** with Li/NH_3 gave *endo*-bicyclo[4.1.0]heptan-2-ol (**1b**), which had identical spectral and chromatographic properties as a sample prepared by Simmons–Smith reaction of 2-cyclohexenol.[1] Analogous reduction of exo alcohol **2a** gave *exo*-bicyclo[4.1.0]heptan-2-ol (**2b**) which had an NMR spectrum identical with that published.[4]

***endo*- and *exo*-6,6-Dichloro-5-methylbicyclo[3.1.0]hexan-2-ols (3a and 4a).** Reaction of 3-methyl-2-cyclopentenol (20 mmol) with dichlorocarbene by the general procedure gave 3.1 g (85%) of adducts **3a** and **4a** as an oily solid. GC and NMR analysis of the mixture indicated this to be 70% endo alcohol **3a** and 30% exo alcohol **4a**. Recrystallization from hexane gave endo alcohol **3a** as a white solid: mp 80–81 °C; NMR ($CDCl_3$) δ 4.67–5.16 (m, CHOH), 1.47 (s, CH_3). Anal. Calcd for $C_7H_{10}Cl_2O$: C, 46.43; H, 5.57; Cl, 39.16. Found: C, 46.66; H, 5.60; Cl, 38.93.

Reduction of endo alcohol **3a** with Li/NH_3 gave *endo*-5-methylbicyclo[3.1.0]hexan-2-ol (**3b**), which had an NMR spectrum identical with that published.[6]

***endo*- and *exo*-7,7-Dichloro-6-methylbicyclo[4.1.0]heptan-2-ols (5a and 6a).** Reaction of 3-methyl-2-cyclohexenol (24 mmol) with dichlorocarbene by the general procedure gave 3.02 g (72%) of adducts **5a** and **6a** as a white solid. GC and NMR analysis of the mixture indicated this to be 94% endo alcohol **5a** and 6% exo alcohol **6a**. Recrystallization from hexane gave endo alcohol **5a** as a white solid: mp 65–66 °C; NMR ($CDCl_3$) δ

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3.84–4.50 (m, CHOH), 1.46 (s, CH_3). Anal. Calcd for $C_8H_{12}Cl_2O$: C, 49.25; H, 6.20; Cl, 36.35. Found: C, 49.05; H, 6.18; Cl, 36.51.

Reduction of endo alcohol **5a** with Li/NH_3[5] gave *endo*-6-methylbicyclo[4.1.0]heptan-2-ol (**5b**), which had an NMR spectrum identical with that published.[7]

***exo*-8,8-Dichlorobicyclo[5.1.0]octan-2-ol (7a).** Reaction of 2-cycloheptenol (20 mmol) with dichlorocarbene by the general procedure gave 1.54 g (40%) of exo alcohol **7a** as a solid. Recrystallization from hexane gave material with mp 75–75.5 °C (lit.[4] mp 74.5–75.5 °C); NMR ($CDCl_3$) δ 3.44–3.86 (m, CHOH).

Reduction of exo alcohol **7a** with Li/NH_3[5] gave *exo*-bicyclo-[5.1.0]octan-2-ol (**7b**), which had an NMR spectrum identical with that published.[4]

***exo*-9,9-Dichlorobicyclo[6.1.0]nonan-2-ol (8a).** Reaction of 2-cyclooctenol (20 mmol) with dichlorocarbene by the general procedure gave exo alcohol **8a**. Recrystallization from hexane gave 3.10 g (74%) of white solid: mp 87–88 °C (lit.[4] mp 87.5–89 °C); NMR ($CDCl_3$) δ 3.34–3.84 (m, CHOH).

Reduction of exo alcohol **8a** with Li/NH_3[5] gave *exo*-bicyclo-[6.1.0]nonan-2-ol (**8b**), which had an NMR spectrum identical with that published.[4]

Registry No. 1a, 73378-12-8; **1b**, 7432-49-7; **2a**, 31022-86-3; **2b**, 31022-87-4; **3a**, 73378-13-9; **3b**, 41299-39-2; **4a**, 73378-14-0; **5a**, 73378-15-1; **5b**, 13388-57-3; **6a**, 73378-16-2; **7a**, 31022-91-0; **7b**, 6142-49-0; **8a**, 31022-98-7; **8b**, 29783-12-8; 2-cyclohexenol, 822-67-3; dichlorocarbene, 75-09-2; 3-methyl-1-cyclopentenol, 3718-59-0; 3-methyl-2-cyclohexenol, 21378-21-2; 2-cycloheptenol, 4096-38-2; 2-cyclooctenol, 3212-75-7.

Restricted Rotation in Pentaarylpyridines. Steric Requirement of the Nitrogen Lone Pair

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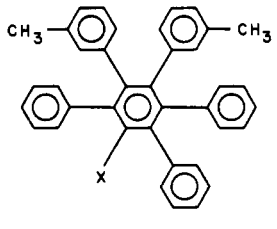
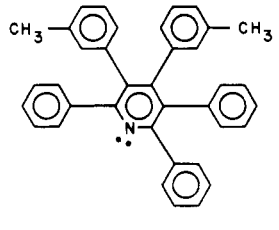
Received January 30, 1980

A perennial unresolved stereochemical question concerns the steric "size" of the nonbonding pair of electrons on nitrogen.[1] One very useful measure of the steric requirement of a group has been the *A* value, or $-\Delta G°$ for the axial–equatorial equilibrium in cyclohexane derivatives.[2] As a result, many attempts to measure $-\Delta G°$ for the lone pair in piperidine have been made. However, there is not as yet complete agreement as to whether this molecule is most stable with the nitrogen lone pair in the axial or in the equatorial position.[3]

We have recently shown[6] that substituted pentaphenylbenzenes such as those represented by **1** exist in a



1



2

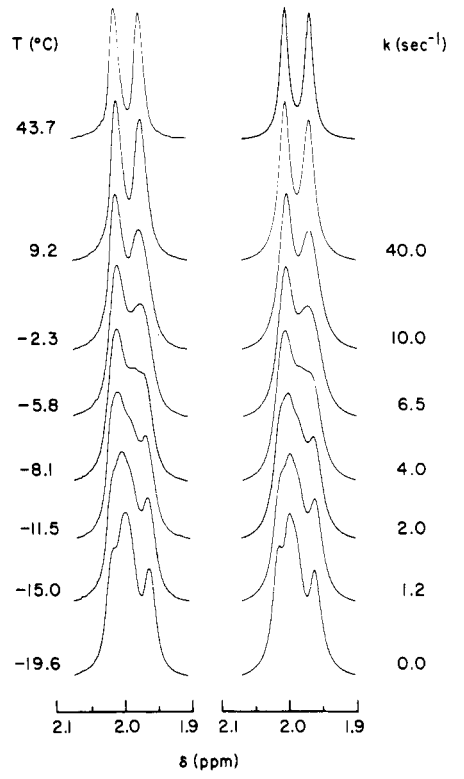


Figure 1. Experimental (left) and calculated (right) 100-MHz ^1H NMR spectra for **2** in chloroform-*d* solution at selected temperatures.

perpendicular conformation with the five peripheral aryl rings approximately at right angles to the plane of the central ring on the NMR time scale. These molecules display restricted rotation about the bonds joining the central ring and the peripheral rings bearing meta methyl groups. Results for a variety of substituents X revealed that substantial steric buttressing effects are transmitted from X to the vicinity of the rotating rings. The free energies of activation for rotation ($\Delta G^{\ddagger}_{293}$) ranged from 15.5 to 18.7 kcal/mol and were linearly related to $-\Delta G°$ for the same substituent X in the axial–equatorial cyclohexane equlibrium (eq 1). This relationship suggests that steric

$$\Delta G^{\ddagger}_{293} = 0.60(-\Delta G°) + 15.4 \quad (1)$$

buttressing interactions in the pentaarylbenzenes are similar in their general nature to steric effects in the cyclohexanes and that values for $-\Delta G°$ may be estimated from energy barriers in the pentaarylbenzene system.[6]

It has been known for some time[7] that pentaphenylpyridine can be prepared by a route similar to that employed for pentaphenylbenzenes.[6] Because pentaphenylpyridine in both its free base and protonated forms closely resembles the pentaarylbenzenes such as **1** in stereochemistry and steric properties, a properly substituted pentaarylpyridine would appear to be an ideal molecule in which to compare the steric requirements of hydrogen and the nitrogen lone pair.

Pentaarylpyridine **2** (mp 208.5–210 °C) was prepared by heating 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone[8,9] with an excess of benzonitrile at 380 °C for 18 h in a sealed tube. Purification of the product was

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