(0.15 mole) of silver nitrate in 150 ml of anhydrous ethyl ether was added 14 g (0.1 mole) of dextrorotatory α-phenylethyl chloride ($\alpha^{25}D$ +37.04°, $n^{20}D$ 1.5271) over a period of 1 hr. The reaction was conducted at room temperature for an additional 6 hr. The resulting mixture was filtered and the silver salts were washed with fresh ether. Distillation gave 13.6 g (82% yield) of dextrorotatory α-phenylethyl nitrate, $\alpha^{25}D$ +3.78°, $n^{20}D$ 1.5089, bp 60–63° (1 mm). *Anal.* Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43. Found: C, 57.63; H, 5.41.

B. In Acetonitrile. Another 14-g sample of the dextrorotatory α-phenylethyl chloride ($\alpha^{25}D$ +37.04°) employed in A was added to a solution of 25.6 g of silver nitrate in 150 ml of acetonitrile in 1 hr After stirring for 20 hr at room temperature, on working up, there was obtained 13.72 g (82% yield) of levorotatory α-phenylethyl nitrate, $\alpha^{25}D$ −6.05°, $n^{20}D$ 1.5088, bp 57–59° (1 mm). *Anal.* Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43. Found: C, 57.42; H, 5.22.

C. In Petroleum Ether. To a stirred suspension of 27.5 g of silver nitrate in 100 ml of petroleum ether (bp 35–37°) was added 15.11 g of levorotatory α-phenylethyl chloride, $\alpha^{25}D$ −10.62°, $n^{20}D$ 1.5272, in 30 min. After 24 hr of stirring at room temperature, the reaction mixture was worked up. Distillation gave 16.92 g (95% yield) of dextrorotatory α-phenylethyl nitrate, $\alpha^{26}D$ +1.63°, $n^{20}D$ 1.5089, bp 55–56° (1 mm). *Anal.* Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.27; H, 5.37; N, 8.36.

D. In Benzene. In 30 min, 14 g of levorotatory α-phenylethyl chloride ($\alpha^{27}D$ −35.64°, $n^{20}D$ 1.5271) was added to a stirred suspension of 25.6 g of silver nitrate in 100 ml of benzene. After stirring for 6 hr at room temperature and working up there was obtained 15.67 g (94% yield) of levorotatory α-phenylethyl nitrate, $\alpha^{27}D$ −1.80°, $n^{20}D$ 1.5088. *Anal.* Calcd for $C_8H_9NO_3$: N, 8.38. Found: N, 8.70.

Reaction of α-Phenylethyl Chloride with Silver Fluoroborate. Silver fluoroborate (1.66 g, 0.03 mole) was dissolved in 5 ml of acetonitrile and 2.8 g (0.02 mole) of α-phenylethyl chloride was added. The reaction mixture became somewhat warm and a precipitate formed. After 45 min at room temperature, ice was added and when it had melted the solution was ether extracted. The extracts were dried over anhydrous magnesium sulfate and concentrated, and the residue was distilled. Thirty per cent (0.83 g) of the α-phenylethyl chloride was recovered. Following this, 0.51 g (45% yield) of a liquid, bp 120–125° (1 mm), was obtained which, on seeding with N-α-phenylethylacetamide, crystallized, mp 76–77°. Authentic N-α-phenylethylacetamide, prepared according to Gotze,[31] had mp 75.6–76.5°.

Reaction of *t*-Butyl Chloride with Silver Nitrite.[32] To 79 g of silver nitrite in 200 ml of acetonitrile at 0°, 46.3 g of *t*-butyl chloride was added dropwise, with stirring, over a period of 2 hr. A precipitate formed at once; after 3 hr at 0° the system was allowed to come to room temperature. Finally, after 1 more day, the silver salts were isolated and the filtrate was distilled. This gave 10 g (17% yield) of N-*t*-butylacetamide, mp 99–100°.

The Solubility of Silver Nitrate in Organic Solvents.[8] Silver nitrate (20.0 g) was extracted[5] with cyclohexane for 5 days at 18–20° (*ca.* 40 ml of fresh solvent every 5 min). There was no loss in weight for the thimble and the sodium bromide test for silver[5] was negative. A duplicate experiment using anhydrous ethyl ether again showed that no silver nitrate had dissolved. However, when 23.0 g of silver nitrate was extracted with benzene (5 days, 18–20°, *ca.* 40 ml of fresh solvent every 5 min) it was found that 24 mg of silver nitrate had been extracted.

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Molecular Asymmetry. VI. The Resolution of Ethyl *p*-Tolyl Sulfoxide[1]

Arthur C. Cope and Edward A. Caress

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received November 22, 1965*

Abstract: Resolution of ethyl *p*-tolyl sulfoxide has been accomplished *via* platinum complexes containing optically active α-methylbenzylamine. Fractional crystallization to constant rotation of the complex containing (+)-α-methylbenzylamine afforded (+)-*trans*-dichloro(ethyl *p*-tolyl sulfoxide)(α-methylbenzylamine)platinum(II) (**1a**), $[\alpha]^{25}D$ +84.7°. In a similar manner, the complex containing (−)-α-methylbenzylamine afforded (−)-*trans*-dichloro(ethyl *p*-tolyl sulfoxide)(α-methylbenzylamine)platinum(II) (**2a**), $[\alpha]^{25}D$ −84.6°. Decomposition of the enantiomeric complexes with aqueous sodium cyanide afforded optically active ethyl *p*-tolyl sulfoxide, $[\alpha]^{25}D$ −203.6° and $[\alpha]^{25}D$ +203.2°, respectively.

The resolution of *trans*-cycloalkenes[2,3] *via* platinum complexes containing optically active α-methylbenzylamine has been extended to include the use of platinum complexes as resolving agents for sulfoxides.

The theoretical[4,5] and synthetic aspects[5,6] of optically active sulfoxides are well known. Until recently, the only methods available for the preparation of optically active sulfoxides have been the oxidation of the corresponding sulfide with an optically active peracid[7] and

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resolution by means of an acidic or basic group present in the structure[8] or by means of a fermentation technique.[9] In general the optical yields in these reactions are poor. Andersen[6] has developed an asymmetric synthesis of sulfoxides, based on the reaction of an optically active sulfinate ester with a Grignard reagent, which gives high optical purity. The chemical racemization of optically active sulfoxides has also been reported.[10] This paper reports the resolution of ethyl *p*-tolyl sulfoxide *via* the complex (+ or −)-*trans*-dichloro(ethyl *p*-tolyl sulfoxide)(α-methylbenzylamine)-platinum(II).

The formation of dimethyl sulfoxide–transition metal complexes is well known.[11-13] Dichlorobis(dimethyl sulfoxide)platinum(II) has been prepared as well as other similar compounds.[11] However, no report of a platinum complex containing both a sulfoxide and an amine ligand was found.

For the resolution of ethyl *p*-tolyl sulfoxide, *trans*-dichloro(ethyl *p*-tolyl sulfoxide)(α-methylbenzylamine)-platinum(II)[14] was prepared according to the procedure previously described for the preparation of the platinum complex of *trans*-cyclooctene.[2,15] Treatment of (+

$$PtCl_2(C_2H_4)(\overset{*}{R}NH_2) + R_1SOR_2 \longrightarrow PtCl_2(R_1SOR_2)(\overset{*}{R}NH_2) + H_2C{=}CH_2$$

1a, 1b and 2a, 2b

$$R_1SOR_2 = C_2H_5SOC_6H_4CH_3\text{-}p$$

or −)-*trans*-dichloro(ethylene)(α-methylbenzylamine)-platinum(II) with ethyl *p*-tolyl sulfoxide effected displacement of ethylene in a slow reaction and afforded the corresponding sulfoxide–amine–platinum complexes **1a**, **1b** and **2a**, **2b**.

When (+)-α-methylbenzylamine was used, the reaction mixture contained the diastereoisomeric *trans*-dichloro[(−)-ethyl *p*-tolyl sulfoxide][(+)-α-methylbenzylamine]platinum(II) (**1a**) and *trans*-dichloro[(+)-ethyl *p*-tolyl sulfoxide][(+)-α-methylbenzylamine]platinum(II) (**1b**). Fractional crystallization of these complexes from methylene chloride–benzene–pentane afforded complex **1a** as the less soluble isomer, $[\alpha]^{25}D$ +84.7°.[16] A similar pair of diastereoisomers was obtained with (−)-α-methylbenzylamine; the less soluble isomer was *trans*-dichloro[(+)-ethyl *p*-tolyl sulfoxide][(−)-α-methylbenzylamine]platinum(II) (**2a**), $[\alpha]^{25}D$ −84.6°.[14]

Complexes **1a** and **2a** were decomposed with aqueous sodium cyanide solution as previously described.[2] Distillation of the sulfoxide obtained on decomposition of complex **1a** gave (−)-ethyl *p*-tolyl sulfoxide, $[\alpha]^{25}D$ −203.6°. Decomposition of complex **2a** gave (+)-ethyl *p*-tolyl sulfoxide, $[\alpha]^{25}D$ +203.2°. (−)-Ethyl *p*-tolyl sulfoxide was found to be optically stable to the conditions employed for the liberation from the platinum complex. The nuclear magnetic resonance spectrum of the (−)-sulfoxide was in agreement with that reported[5] for (+)-ethyl *p*-tolyl sulfoxide. The (+ and −)-sulfoxides had identical solution infrared spectra; both spectra were identical with the spectrum of racemic ethyl *p*-tolyl sulfoxide.

The resolved platinum complexes **1a** and **2a** also had identical infrared spectra. In the infrared spectrum of ethyl *p*-tolyl sulfoxide, the sulfur–oxygen stretching frequency occurs at 1050 cm^{-1}; in the platinum complex this was shifted to 1110 cm^{-1}. A similar shift for dichlorobis(dimethyl sulfoxide)platinum(II) has been reported.[11a] On the basis of the direction of the shift, it has been suggested[11a] that the platinum atom was bound to the sulfur atom rather than to the oxygen atom.

(+)-Ethyl *p*-tolyl sulfoxide, prepared by asymmetric synthesis, had $[\alpha]^{25}D$ +186°[6c] and $[\alpha]D$ +187.5°.[5] The absolute configuration about the sulfur atom in this sulfoxide has been assigned as (*R*).[5]

Experimental Section[17]

Ethyl *p*-Tolyl Sulfoxide. Ethyl *p*-tolyl sulfide[18] (15.2 g, 0.10 mole) was oxidized with sodium metaperiodate according to the procedure of Leonard and Johnson.[19] The sulfoxide, bp 104.0–105.5° (0.4 mm) (lit bp 94° (0.4 mm)[5] and bp 123–126° (1.5 mm)[6c]), was obtained in 70% yield.

(+)-*trans*-Dichloro(ethyl *p*-tolyl sulfoxide)(α-methylbenzylamine)-platinum(II) (1a). To a cooled solution of 30 g (0.072 mole) of (+)-*trans*-dichloro(ethylene)(α-methylbenzylamine)platinum(II)[2,20] in 100 ml of methylene chloride was added a cooled solution of 12.1 g (0.072 mole) of ethyl *p*-tolyl sulfoxide in 30 ml of methylene chloride. The solution was allowed to stand for 36 hr. After removal of the solvent at reduced pressure, a viscous, orange oil was obtained. Fractional crystallization of the diastereoisomers from benzene–pentane afforded yellow crystals. Additional fractions were obtained by similar treatment of the mother liquor. These fractions were recrystallized by dissolution in the minimum amount of methylene chloride and addition of an equal volume of benzene, followed by addition of a sufficient amount of pentane to bring the solution to the cloud point. Complex **1a** (7.43 g, 37%) thus obtained had mp 186–195° dec. After four recrystallizations, complex **1a** had $[\alpha]^{25}_{578}$ +89.9°, $[\alpha]^{25}_{546}$ +105.7°, $[\alpha]^{25}D$ +85.1° (*c* 1.39, methylene chloride); after eight recrystallizations, $[\alpha]^{25}_{578}$ +89.2°, $[\alpha]^{25}_{546}$ +103.9°, $[\alpha]^{25}D$ +84.7° (*c* 0.51, methylene chloride).

Anal. Calcd for $C_{17}H_{23}Cl_2NOPtS$: C, 36.75; H, 4.17; Cl, 12.76; N, 2.52; Pt, 35.14; S, 5.77. Found: C, 36.98; H, 4.13; Cl, 12.62; N, 2.33; Pt, 35.92; S, 5.77.

(−)-*trans*-Dichloro(ethyl *p*-tolyl sulfoxide)(α-methylbenzylamine)-platinum(II) (2a). A cooled solution of 41.5 g (0.10 mole) of (−)-*trans*-dichloro(ethylene)(α-methylbenzylamine)platinum(II)[2,21] in 130 ml of methylene chloride was treated with a cooled solution of 16.8 g (0.10 mole) of ethyl *p*-tolyl sulfoxide in 37 ml of methylene chloride and the reaction mixture was allowed to stand for 36 hr. The solvent was removed at reduced pressure and the diastereoisomers were separated by fractional crystallization as described above for complex **1a**. Complex **2a** (1.51 g, 5%), mp 194–196° dec, had $[\alpha]^{25}_{578}$ −87.2°, $[\alpha]^{25}_{546}$ −102.3°, and $[\alpha]^{25}D$ −82.7°

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(15) The asterisk above the amine indicates that (+ or −)-α-methylbenzylamine was used.

(16) The complexes **1a** and **2a** were recrystallized to constant rotation and were pure diastereoisomers according to this criterion.

(17) Optical rotations were measured with a Zeiss photoelectric precision polarimeter. The rotations measured at 546.1 and 577.8 mμ were used to calculate the value at the sodium D line (589.2 mμ). Melting points were taken on a Kofler hot stage; boiling points are uncorrected. Analyses were performed by Dr. S. M. Nagy.

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(21) The (−)-α-methylbenzylamine used in the preparation of this complex had $[\alpha]^{25}D$ −37.71° (neat, d^{25}_4 0.9528).

(c 2.38, methylene chloride) after four recrystallizations; after seven recrystallizations, $[\alpha]^{25}_{578}$ −87.8°, $[\alpha]^{25}_{546}$ −101.5°, $[\alpha]^{25}D$ −83.5° (c 1.35, methylene chloride); and after ten recrystallizations the rotation was $[\alpha]^{25}_{578}$ −89.0°, $[\alpha]^{25}_{546}$ −103.4°, $[\alpha]^{25}D$ −84.6° (c 1.32, methylene chloride). The solution infrared spectra (chloroform) of complexes **1a** and **2a** were identical.

Anal. Calcd for $C_{17}H_{23}Cl_2NOPtS$: C, 36.75; H, 4.17; Cl, 12.76; N, 2.52; Pt, 35.14; S, 5.77. Found: C, 36.83; H, 4.13; Cl, 12.59; N, 2.63; Pt, 34.75; S, 5.72.

(−)-Ethyl *p*-Tolyl Sulfoxide. A solution of 6.0 g (0.011 mole) of (+)-*trans*-dichloro(ethyl *p*-tolyl sulfoxide)(α-methylbenzylamine)platinum(II) (**1a**) in 120 ml of methylene chloride was treated with 120 ml of a 10% aqueous sodium cyanide solution as described previously.[2] The reaction mixture was worked up as described and the solvent was removed at reduced pressure. Distillation of the resulting yellow oil gave 1.27 g (70%) of (−)-ethyl *p*-tolyl sulfoxide, bp 76–77° (0.01 mm), $[\alpha]^{25}_{578}$ −214.5°, $[\alpha]^{25}_{546}$ −250.5°, and $[\alpha]^{25}D$ −203.6° (c 0.93, acetone). The nmr spectrum of this material was identical with that previously described[5] for (+)-ethyl *p*-tolyl sulfoxide.

Anal. Calcd for $C_9H_{12}OS$: C, 64.24; H, 7.19; S, 19.06. Found: C, 63.91; H, 7.44; S, 18.87.

(+)-Ethyl *p*-Tolyl Sulfoxide. (−)-*trans*-Dichloro(ethyl *p*-tolyl sulfoxide)(α-methylbenzylamine)platinum(II) (**2a**) (1.0 g, 0.0018 mole) in 20 ml of methylene chloride was treated with 20 ml of a 10% aqueous sodium cyanide solution as described above. The solvent was removed under reduced pressure to give a yellow oil, which upon distillation gave 0.063 g (21%) of (+)-ethyl *p*-tolyl sulfoxide, $[\alpha]^{25}_{578}$ +214.2°, $[\alpha]^{25}_{546}$ +250.0°, and $[\alpha]^{25}D$ +203.2° (c 0.60, acetone). The infrared spectrum of the (+)-sulfoxide was identical with that of the (−)-sulfoxide; both were identical to that of *dl*-ethyl *p*-tolyl sulfoxide.

Anal. Calcd for $C_9H_{12}OS$: C, 64.24; H, 7.19; S, 19.06. Found: C, 64.14; H, 7.27; S, 19.36.

Conformational Study of Cyclohexanols in Dimethyl Sulfoxide

Charles P. Rader

Contribution from the Research Department, Organic Chemicals Division, Monsanto Company, St. Louis, Missouri 63166. *Received November 3, 1965*

Abstract: Proton magnetic resonance spectra of epimeric cyclohexanols in dimethyl sulfoxide reveal that in all cases the hydroxyl proton of the axial alcohol resonates at higher field than the equatorial one. The spin–spin coupling between the hydroxyl and carbinol protons is found to be greater for the equatorial epimer. This difference in coupling is readily related to the effect of dihedral angle upon the coupling constant and the different populations of rotational isomers about the C–O bond. Factors other than the relative strength of the axial and equatorial O–H---DMSO hydrogen bonds appear to influence the chemical-shift difference, since infrared data show cyclohexanol and each of the 4-*t*-butylcyclohexanols to form with DMSO hydrogen bonds of comparable strength. Further structural applications of the magnitude of the hydroxyl–carbinol proton coupling are discussed.

Proton magnetic resonance (pmr) spectra of alcohols are known to show spin–spin coupling between hydroxyl and carbinol protons, provided there is an extremely low concentration ($<10^{-5}$ M) of acids or bases which catalyze O–H proton exchange. It is generally more difficult to observe this coupling in nonpolar solvents[1] than in polar ones which can donate an electron pair to the hydroxyl group.[2] It is reasonable to presume[3] that hydrogen bond formation increases the O–H proton lifetime on a single molecule sufficiently to permit splitting of its resonance signal to be observed.

Dimethyl sulfoxide (DMSO) has been found to be an excellent solvent for the facile observation of H–C–O–H splitting. In DMSO Chapman and King[4] have shown that pmr spectra of alcohols may be used for classification purposes according to the multiplicity of the O–H resonance. More recently the use of DMSO as solvent for pmr studies of OH groups of sugars has been reported.[5]

This paper reports a study of hydroxyl proton chemical shifts and coupling constants for a series of epimeric cyclohexanols in DMSO and the structural correlation of these parameters. The relationship between vicinal coupling constants and dihedral angle for H–C–C–H systems is well established[6] and has been extremely useful in conformational studies. It is reasonable to expect H–C–O–H coupling constants to vary with dihedral angle in a manner similar to that for H–C–C–H systems. Thus, one should be able to correlate the magnitude of carbinol–hydroxyl proton splitting with the rotational conformations of the OH group. These nmr results should complement previous infrared studies[7] of conformational equilibria resulting from rotation about the C–O bond of alcohols.

Results

For reasons previously mentioned,[4] DMSO was found to be a superior solvent for the study of hydroxyl pmr spectra of alcohols. In dilute DMSO the OH proton resonance occurs in the τ 5.5–6.3 region, a

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