[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Attempted Resolution of Phenyl-d_5-phenylaminomethane

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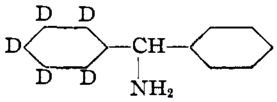
The resolution of phenyl-d_5-phenylaminomethane I by Clemo and McQuillen[1] has remained the only example of a compound of the type $RR'CX_HX_D$ which has been obtained optically active in spite of extensive work on the stereochemistry of a variety of deuterium compounds.[2] Since the available evidence leads to the deduction that the optical activity of such a compound would be extremely small, if measurable at all, whereas the rotations of the two forms of phenyl-d_5-phenylaminomethane were reported as $[\alpha]$ −5.7° and +5.0°, it seemed advisable to repeat this work. The constants reported for the heavy benzene used in the investigation just cited indicated the material to be of doubtful purity;[3] moreover, the amount of the heavy benzene available was so small that experimentation was rendered difficult.



I

In the present research a particular effort was made to ascertain the purity of the hexadeuterobenzene. It was prepared by the method of Klit and Langseth[4] which consists in the exchange reaction between deuterium chloride and benzene with aluminum chloride as catalyst. The sample used had a density d^{25}_{25} 0.9404, corresponding to 92.5% of the theoretical amount of deuterium,[5] and a freezing point of +6.5°. The amount of hydrogen present in the benzene would not affect the resolvability of the derivative prepared from it, although this derivative might not possess the maximum rotation which would be obtained from 100% hexadeuterobenzene.

The heavy benzene was converted by the procedure described by Clemo[1] to phenyl-d_5-phenylaminomethane. A Friedel and Crafts reaction with benzoyl chloride gave pentadeuterophenyl phenyl ketone; the oxime of this was then prepared and reduced with sodium amalgam to the amine. Resolution was attempted through two different salts. The *d*-tartrate ($[\alpha]_D$ +12.5°) was obtained in essentially quantitative yield and its rotation did not change during a series of fourteen crystallizations from alcohol. The amine obtained by decomposition of the purest tartrate showed no activity. The *d*-3-bromocamphor-8-sulfonate, which had the distinct advantage over the tartrate of possessing a specific rotation nearly five times as large ($[\alpha]_D$ +62.1°) was also formed in essentially quantitative yield by the reaction of the amine hydrochloride and ammonium bromocamphor sulfonate. Crystallization several times from water did not alter the rotation of the salt and the hydrochloride of the amine obtained by decomposition of the sulfonate showed no optical activity.

The absence of activity in the product makes it appear possible that the relatively impure heavy benzene used by Clemo and McQuillen may have vitiated their results. Optically inactive material might result from symmetrical distribution of the deuterium between the two phenyl groups in our heavy benzophenone through interchange of hydrogen and deuterium during the preparation of the ketone. This possibility, however, seems very remote. Clemo has indicated his intention of establishing the exact facts by study of the Beckmann rearrangement product of the oxime.

In view of the results described in this communication, the establishment of optical activity in a molecule of the type $RR'CX_HX_D$ is left uncertain and a further experimental study of this problem is desirable.

The density of the "heavy" benzophenone (d^{61}_4 1.109) as determined by the method previously used for deuterium compounds,[2,6] was about 2.5% greater than that of ordinary benzophenone (d^{61}_4 1.084; Perkin[7] reports d^{60}_4 1.078).

Experimental

Preparation of Hexadeuterobenzene.—The exchange reaction was carried out in an all-glass apparatus very similar to that of Klit and Langseth.[4] It was found that a U-tube with arms of unequal size made the most con-

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(1) Clemo and McQuillen, *J. Chem. Soc.*, 808 (1936).

(2) For previous references see McGrew and Adams, THIS JOURNAL, **59**, 1497 (1937).

(3) Ann. Reports of the Chemical Society, 229 (1936).

(4) Klit and Langseth, *Z. physik. Chem.*, **A176**, 65 (1936).

(5) Ingold, Raisin and Wilson, *J. Chem. Soc.*, 915 (1936).

(6) McLean and Adams, THIS JOURNAL, **58**, 804 (1936).

(7) Perkin, *J. Chem. Soc.*, **69**, 1201 (1896).

venient reaction vessel: in the bottom of the large arm, about 20 × 150 mm., were placed the catalyst, a few grams of resublimed aluminum chloride supported on glass wool, and the stream of deuterium chloride was bubbled up through the benzene and catalyst. Since the aluminum chloride gradually dissolves in the benzene, it was found advisable to use only a small amount of catalyst, otherwise much benzene was retained in the black viscous mass after the reaction was completed.

The effluent hydrogen chloride and deuterium chloride mixture was passed through a tube packed with anhydrous sodium carbonate supported on glass wool and heated to 250° by resistance wire. The deuterium was thus recovered as deuterium oxide. The benzene was commercially pure material which was dried and redistilled. The thionyl chloride was purified by distillation from quinoline and linseed oil.

Several preliminary runs using various percentages of heavy water resulted in obtaining a benzene with 60% of the hydrogen replaced by deuterium. This was treated as follows: a mixture of 20 g. of this benzene and 5 g. of freshly sublimed aluminum chloride was placed in the reaction vessel and a stream of deuterium chloride generated from 20 g. of 99.6% deuterium oxide and 140 g. of thionyl chloride was passed through the benzene over a period of thirteen and one-half hours. The catalyst dissolved and the solution darkened.

The reaction mixture was poured into a small distilling flask and 14.5 g. of heavy benzene distilled off, leaving a residue of aluminum chloride. The sample was dried over potassium carbonate to remove water and acid, and redistilled; yield 11.5 g., d^{25}_{25} 0.9404, determined in a pycnometer of 1.5-cc. capacity. The freezing point of the sample was obtained by taking a cooling curve of a sample in a test-tube surrounded by an ice-bath; the value obtained by cooling was +6.4° and by allowing the solid to warm up, 6.5°. Ordinary benzene under the same conditions had a freezing point of 5.5°.

Preparation of Pentadeuterobenzophenone.—A mixture of 1.96 g. of heavy benzene, 5 cc. of carbon disulfide and 3.4 g. of benzoyl chloride was cooled in a freezing mixture, while 4.0 g. of freshly sublimed aluminum chloride was added in several portions. A reflux condenser was attached, the mixture allowed to come to room temperature, and refluxed on the steam-bath for an hour.[8] The reaction mixture was poured into 20 g. of ice and 4 cc. of concentrated hydrochloric acid, and the carbon disulfide distilled off on the steam-bath; it was then boiled under reflux for twenty minutes to decompose unreacted benzoyl chloride and cooled, which caused crystallization of some benzoic acid. The organic material was extracted with ether, the extract washed with dilute alkali, then with water, dried over anhydrous sodium sulfate and the solvent removed. The benzophenone was purified by distillation in a small von Braun flask; yield, 2.15 g. (50% of theoretical) of "heavy" benzophenone, m. p. 47–48°. In other runs better yields than the above were obtained.

The density was determined in a 0.34-cc. pycnometer,[6] using chloroform as the thermostat liquid, d^{61}_4 1.109; ordinary benzophenone, prepared under identical conditions, d^{61}_4 1.084; from Perkin's data[7] d^{60}_4 for benzophenone is 1.078. The value calculated for the density of pentadeuterobenzophenone by the equation of McLean and Adams,[6] allowing for the hydrogen present, is 1.112.

Anal. Calcd. for $C_{13}H_5D_5O$: C, 83.4; H + D, 8.02. Found: C, 83.7; H + D, 7.82.

Pentadeuterobenzophenoneoxime.—To a solution of 1.89 g. of heavy benzophenone in 15 cc. of alcohol, 1.4 g. of hydroxylamine hydrochloride and 1.6 g. of sodium hydroxide, each dissolved in the minimum amount of water, were added. After refluxing for one and one-half hours, the reaction mixture was poured into 40 cc. of water and 10 cc. of concentrated hydrochloric acid, the precipitated oxime filtered off and washed with water. The product weighed 2.03 g., and was pure as obtained with m. p. 142–143°. It can be recrystallized from methanol.

Anal. Calcd. for $C_{13}H_6D_5ON$: C, 77.2; H + D, 7.92. Found: C, 77.4; H + D, 7.40.

Phenyl-d_5-phenylaminomethane.—To a solution of 2.03 g. of the heavy oxime in 10 cc. of alcohol, 40 cc. of 5% aqueous sodium hydroxide and 250 g. of 4% sodium amalgam was added in several portions; after allowing the reaction to run at room temperature for about an hour it was refluxed for four hours, adding 50% acetic acid occasionally through the condenser. The amine gradually appeared on top of the solution as a brown oil, and was removed from the reaction mixture by several ether extractions; the extract was washed with dilute alkali, the ether removed, and 1.82 g. of the amine obtained as a yellow oil.

***d*-Hydrogen Tartrate of Phenyl-d_5-phenylaminomethane.**—A solution of 1.42 g. of *d*-tartaric acid in 5 cc. of water was added to 1.82 g. of the amine, and the salt which precipitated immediately was filtered and dried; yield, 3.06 g. (94%). The melting point was between 175 and 180° with decomposition depending on the rate of heating (Clemo gave m. p. 181°). The salt was recrystallized from about 25 cc. of 95% ethanol, and 2.54 g. was obtained. Rotation: 0.692 g. made up to 15 cc. in water gave in a 1-dm. tube, α^{30} +0.56°, $[\alpha]^{30}\text{D}$ +12.1°.

The tartrate was now recrystallized repeatedly from 95% ethanol, and the rotation measured frequently: since about 80% of the salt was recovered from each crystallization, no attempt was made to work up the filtrates. The specific rotations were essentially unchanged within experimental error, *e. g.*, $[\alpha]^{30}\text{D}$ +12.5°, +12.7°, +12.4°.

The rotations are identical with that found for the *d*-hydrogen tartrate of ordinary diphenylaminomethane made in a similar manner. Rotation: 0.693 g. made up to 15 cc. in water gave in a 2-dm. tube: α^{30} +1.14°, $[\alpha]^{30}\text{D}$ +12.3°.

Hydrolysis of the Tartrate Salt.—A solution of 0.62 g. of pure amine tartrate in 15 cc. of water was treated with 2 cc. of 25% sodium hydroxide, the amine extracted with ether, dried over potassium hydroxide and the solvent removed. Rotation: 0.32 g. made up to 10 cc. in 95% ethanol in a 1-dm. tube gave α^{30} 0.00 ± 0.01.

***d*-Bromocamphorsulfonate of Phenyl-d_5-phenylaminomethane.**—A sample of 2.68 g. of pentadeuterobenzo-

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[8] Clemo heated the reaction mixture for twelve hours, but in preliminary experiments with ordinary benzene it was found that good yields were obtained with one hour's refluxing, and it was desired to avoid as much as possible conditions under which interchange of deuterium and hydrogen might occur.

phenoneoxime was converted to the amine with sodium amalgam. The amine was changed to its hydrochloride by dissolving in ether and passing in hydrogen chloride; yield, 4.3 g. of the crude salt. A small amount of impurity of inorganic material was separated by dissolving the amine salt in ethanol and filtering. The amine hydrochloride (2.48 g.) was obtained by adding ether to the ethanol solution, as a white compound, decomposing about 290°.

A solution of 2.48 g. of the amine hydrochloride in 25 cc. of water was mixed with 3.62 g. of the ammonium salt of *d*-bromocamphorsulfonic acid dissolved in 20 cc. of water. An immediate precipitate of 5.58 g. of salt occurred which was obviously contaminated with a little ammonium bromocamphor sulfonate. After crystallization from about 100 cc. of water, 4.71 g. was obtained. When pure it melted at 237–239° with decomposition. By subsequent crystallizations, no change in rotation was observed. Rotation: 0.482 g. made up to 15 cc. in 95% ethanol in a 2-dm. tube gave α^{30} +3.99°, $[\alpha]^{30}\text{D}$ +62.1°.

The *d*-bromocamphor sulfonate of ordinary diphenylaminomethane has not been described previously. It was prepared in a similar manner as white needles from alcohol, m. p. 236–238° with decomposition.

Anal. Calcd. for $C_{23}H_{28}O_4NBr$: C, 55.8; H, 5.7; neut. equiv., 494. Found: C, 56.0; H, 5.9; neut. equiv., 487. Rotation: 0.505 g. made up to 15 cc. in 95% ethanol gave in a 1-dm. tube, α^{30} + 2.09°, $[\alpha]^{30}\text{D}$ +62.1°.

Decomposition of the Bromocamphorsulfonate of the "Heavy" Amine.—The bromocamphorsulfonate (1.5 g.) was decomposed by dissolving in 50 cc. of dilute alkali, extracting with ether, and washing with dilute sodium hydroxide. The amine hydrochloride was precipitated from the ether by hydrogen chloride and reprecipitated from ethanol with ether; m. p. 286–288° with decomposition. Rotation: 0.20 g. made up to 10 cc. in 95% ethanol in a 1-dm. tube gave α 0.00 ± .01.

Summary

1. Phenyl-d_5-phenylaminomethane was prepared according to the method of Clemo from hexadeuterobenzene of 92.5% purity.

2. This product was converted to the *d*-tartrate and *d*-bromocamphorsulfonate salts.

3. By decomposition of the salts only optically inactive amine was obtained. Uncertainty is thus introduced concerning the resolution of substances of the general type $RR'CX_HX_D$.

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Mercury Derivatives of the *o*-Chlorobenzyl Radical

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In continuing the studies on the electron-sharing ability of organic radicals,[1] the *o*-chlorobenzylmercuric nitrate, the iodide, and the di-*o*-chlorobenzylmercury were desired. Since none of the mercury derivatives of this radical had been reported, the chloride, bromide, acetate, and the benzoate were also prepared.

The bromide and chloride derivatives were prepared by the reaction of the Grignard derivative of the *o*-chlorobenzyl radical with the corresponding mercuric halides. A 75–76% yield of Grignard reagent, as determined by titration,[2] was prepared from 0.1 mole of *o*-chlorobenzyl chloride. To this was added in small amounts 0.185 mole of the dry powdered mercuric halides. The mixture was refluxed and stirred for several hours, the ether was evaporated off, and the crude material washed several times with 250-cc. portions of a 1% acetic acid solution. The crude compounds were extracted and recrystallized from alcohol or benzene. These two derivatives as well as the iodide were also prepared in almost pure state in quantitative yields by boiling equal molecular quantities of di-*o*-chlorobenzylmercury and the corresponding mercuric halide in ethyl alcohol. The iodide crystals turned yellow when exposed to light for a few minutes. The acetate was prepared in a similar manner.

Di-*o*-chlorobenzyl mercury was obtained by treating an excess of the Grignard reagent with dry mercuric chloride. The halide was added in small portions and the mixture was refluxed and stirred for three hours. After the excess Grignard reagent had been hydrolyzed, the ether layer was evaporated, leaving the impure di-*o*-chlorobenzyl mercury, which was recrystallized from alcohol.

The *o*-chlorobenzylmercuric acetate and the benzoate derivatives were obtained by refluxing *o*-chlorobenzylmercuric chloride with slightly more than the theoretical quantity of the corresponding silver salt in alcohol until the clear solutions gave

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(1) Johns with Hixon, THIS JOURNAL, **49**, 1786 (1927); *J. Phys. Chem.*, **34**, 2226 (1930).

(2) Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).