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Preparation of 1,1′- and 5,5′-Bitetralyl

ROBERT H. WILLIAMS
Socony Mobil Oil Co. Inc., Princeton, N. J.

The preparation of 5,5′-bitetralyl (m.p. 93.5–94° C.) by the partial hydrogenation of 1,1′-binaphthyl using a palladium-on-carbon catalyst is described. The main product from the reaction of di-*tert*-butyl peroxide with tetralin (1,2,3,4-tetrahydronaphthalene) is 1,1′-bitetralyl. The identity of the bitetralyls was confirmed by elemental analysis, NMR spectrum, and, in the case of the 1,1′ isomer by dehydrogenation to 1,1′-binaphthyl. The presence of *meso* and *racemic* stereoisomers of 1,1′-bitetralyl was demonstrated.

IN THE COURSE of some studies on the radiolysis of 1,2,3,4-tetrahydronaphthalene (tetralin), two bitetralyls were prepared as standards to aid in the analysis of the polymer. One of these, 5,5′-bitetralyl, had not been described previously and was prepared by the partial hydrogenation of 1,1′-binaphthyl. The other , 1,1′-bitetralyl, had been isolated as a by-product from a Grignard reaction involving 1-bromotetralin (*3*). A more convenient preparative method was to treat tetralin with di-*tert*-butyl peroxide. This is similar to a published method of dimerizing alkylbenzenes using diacetyl peroxide (*1*).

EXPERIMENTAL

Preparation of 5,5′-Bitetralyl. Ten grams of 1,1′-binaphthyl (Aldrich Chemical Co.) in 90 grams of cyclohexane plus two grams of 5% palladium-on-carbon catalyst was hydrogenated in a Paar hydrogenation apparatus at an initial pressure of 40 p.s.i.g. and 65–70° C. After 24 hours an additional two grams of catalyst was added and hydrogenation continued for another 24 hours after repressuring the system to 40 p.s.i.g. The crude hydrogenation product was absorbed on 135 grams of silica gel. Elution with *n*-pentane gave no high boiling eluate, indicating that no bidecalyl was formed. Using benzene, nine grams of eluate was recovered which, upon several recrystallizations from absolute alcohol, gave 5.2 grams of colorless crystals melting at 93.5–94° C. (no literature value reported.) *Anal.*Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.35; H, 8.38.

This isomer differs from 1,1′-bitetralyl in melting point, mass spectrum, and NMR specturm. In the NMR spectrum, there were four fully resolved proton peaks corresponding to aromatic protons (δ = 6.84 ppm), 4,4′ protons (δ = 2.74 ppm), 1,1′ protons (δ = 2.26 ppm), and combined 2,2′ and 3,3′ protons (δ = 1.66 ppm). The observed areas were in the ratio 5.8 : 4.0 : 3.6 : 7.5, which agree very well with the calculated values 6:4:4:8. Analysis of the spectra leading to values of the various coupling constants is not possible due to the poorly resolved structure within the assigned regions of the spectrum.

Preparation of 1,1′-Bitetralyl. A mixture of 132 grams (1.0 mole) of tetralin and 14.6 grams (0.1 mole) of di-*tert*-butyl peroxide was heated in helium atmosphere to 155° C. in a flask equipped with a Dean-Starke type of distilling tube receiver and a reflux condenser. Reflux started shortly thereafter as *tert*-butyl alcohol was formed. When the temperature reached 135° C., the alcohol and some peroxide were removed. The temperature was raised to 155° C. again during this distillation. The total distillate was 8.0 ml. of which 6.5 ml. was *tert*-butyl alcohol. A volume of peroxide equal to the total volume of distillate was added to the reaction mixture and the cycle was repeated. After collecting 26.5 ml. (ca. 0.3 mole) of the alcohol in this manner, the reaction mixture was distilled in a Piros-Glover spinning band column at 10mm. Hg pressure. Thirty grams of a clear, viscous liquid boiling at 223° C. was obtained, and, upon standing, it partially crystallized. Recrystallization from absolute alcohol gave colorless crystals melting at 82° C. [lit. value 83° C. (*3*)]. *Anal.* Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.60; H, 8.42.

The NMR spectrum showed proton peaks corresponding to aromatic hydrogens (δ = 6.97 p.p.m), tertiary hydrogens (δ = 3.37 p.p.m), secondary hydrogens on alpha carbon atoms (δ = 2.65 p.p.m); and secondary hydrogens on beta carbon atoms (δ = 1.77 p.p.m). The observed areas were in ratio 8.9 : 2.4 : 4.1 : 7.5, which are in good agreement with the calculated values 8:2:4:8. J-values could not be determined for the same reason cited under the previous preparation.

Dehydrogenation of the product with palladium-oncharcoal gave colorless crystals, melting at 154–156° C. This melting range corresponds with the range of values (154–160° C.) reported for 1,1′-binaphthyl and not with the 2,2′ isomer (m.p. 187° C.) nor the 1,2′ isomer (m.p. 79° C.). A mixture melting point with an authentic sample of 1,1′-binaphthyl was undepressed.

The 1,1′-bitetralyl should exist as the *meso* form and a *racemic* modification. The stereochemical composition of dimers of alkylbenzenes has been determined by gas chromatography (*2*). Using a similar column (1.5 meter column of Apiezon L on firebrick at 250° C.), the crystalline 1,1′-bitetralyl showed only a single well defined peak. The unrecrystallized distillate, however, showed two distinct peaks of approximately the same area. Adding a portion of the crystalline product to the liquid distillate reinforced the peak which emerged first. This indicated that during the recrystallization step one stereoisomer had been separated from the other. The mass spectrum of the liquid product was that characteristic of 1,1′-bitetralyl (very weak parent peak, major peak at $m/e = 260$, very intense fragment peak at $m/e = 130$) which shows that the second peak on the chromatogram is not another bitetralyl isomer such as the 2,2′- or 5,5′-bitetralyl which have strong parent peaks. The NMR spectrum of the liquid distillate also confirmed the 1,1′- linkage of the unrecrystallized distillate fraction. There were minor differences in the mass spectrum and the NMR spectrum between the crystalline product and the liquid distillate which were attributed to intrinsic differences between the stereoisomers. As expected, neither fraction was optically active. It is not known whether the crystalline product is *meso* or *racemic*.

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Determination of Virial Coefficients by the Burnett Method

ALAN E. HOOVER, FRANK B. CANFIELD,[1] RIKI KOBAYASHI, and THOMAS W. LELAND, Jr.
William Marsh Rice University, Houston, Texas

Two methods of determining second and third virial coefficients with the Burnett apparatus are described. The first method is an improved way of determining the apparatus constant used in obtaining compressibility factors. The virials are then obtained from these compressibility factors in the conventional manner. The second method avoids the determination of the apparatus constant and furnishes the virial coefficients directly from the experimental data. This method is more accurate if the lowest pressures measured contain non random errors. Second and third virial coefficients for helium and nitrogen are compared by the two methods.

A METHOD for determining the volumetric behavior of gases which requires the measurement of only temperature and pressure on successive isothermal expansions was introduced by Burnett 1936 (*1*). Since its conception this expansion method has been applied by several investigators to measure compressibility over a wide range of temperature and pressure conditions (*2, 10, 15, 16, 19, 21*). Although its principal use has been for compressibility factors, the method has some attractive features for the evaluation of virial coefficients. It avoids not only the difficulties of precise measurement of volumes but also eliminates some of the uncertainties caused by adsorption encountered in the traditional low pressure volumetric methods. The virial coefficients can always be calculated from the compressibility factors, but the Burnett method as used earlier has required the evaluation of an apparatus constant which is a function of the cell volumes. This apparatus constant is evaluated from the measured pressure and temperature data on a nearly ideal gas such as helium. These compressibility factors involve the apparatus constant raised to a power equal to the number of expansions. The evaluation of this constant requires a separate experimental investigation of great precision. The purpose of this paper is to show that virial coefficients and compressibility factors can be obtained directly from the pressure measurements on the unknown gas without requiring the evaluation of the apparatus constant and additional source of error which this entails. This procedure is limited to pressures at which the contribution of the fourth and higher virials is negligible. This means that the initial pressures at which the expansion begins must be slightly lower than when the apparatus constant method is used.

APPARATUS CONSTANT METHOD OF OBTAINING VIRIAL COEFFICIENTS

The Burnett apparatus consists of two vessels of unspecified volume connected to each other by means of an

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[1] Present address: University of Oklahoma, Norman, Okla.