tions it seems that equation (E) ought to be useful for calculating Langmuir isotherms of van der Waals adsorption at one temperature from those at another.

TABLE V

VALUES OF v_m FOR ADSORPTION ISOTHERMS ON CHARCOAL

Gas	Temp., °C.	Curve in Fig. 5	v_m, cc./g.	Surface in sq. m./g. Solid packing	Surface in sq. m./g. Liquid packing
N_2	−195.8	4	181.5	677	795
N_2	−183	1	173.0	646	795
A	−195.8		215.5	746	804
A	−183	5	215.5	746	839
O_2	−183	6	234.6	767	894
CO	−183	3	179.5	665	820
CO_2	− 78	2	185.5	707	853
C_4H_{10}	0		63.0	545	546

Summary

1. A critical discussion of the polarization theory of multimolecular adsorption is presented. It is shown that the adsorption energy due to attraction of dipoles induced into a non-polar gas like argon is insufficient to constitute a major portion of the binding energy between adsorbed layers.

2. Derivation of adsorption isotherm equations for multimolecular adsorption are carried out on the assumption that the same forces that produce condensation are also responsible for multimolecular adsorption.

3. Numerous applications of the equations are given to experimental adsorption isotherms obtained by other investigators as well as by us.

WASHINGTON, D. C. RECEIVED NOVEMBER 19, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY AND THE COLLEGE OF THE CITY OF NEW YORK]

The Synthesis of 1,4-Dimethylphenanthrene by Cyclodehydration Methods

BY DOMENICK PAPA, DAVID PERLMAN AND MARSTON T. BOGERT

In a recent article, Akin, Stamatoff, and Bogert[1] reported the synthesis of 1,4-dimethylphenanthrene from *p*-xylene by the familiar Pschorr reaction, in which they obtained a product quite different from that secured from the same initial material by Bardhan and Sengupta,[2] by another series of reactions, and to which the latter investigators assigned the same constitution.

The experimental results published by Akin, Stamatoff, and Bogert indicated, however, that the Bardhan and Sengupta hydrocarbon was probably the 1,3-dimethyl isomer, previously prepared by Bogert and Stamatoff,[3] and by Haworth, Mavin, and Sheldrick.[4]

At the time, it was suggested by Akin, Stamatoff, and Bogert, although they could not rearrange their own product to the 1,3-dimethyl isomer by selenium fusion, that perhaps something of this kind had happened in the final step of the Bardhan and Sengupta synthesis. We have therefore synthesized the 1,4-dimethylphenanthrene by two slightly different methods, from *p*-xylylethyl cyclohexanols, dehydrogenating the resulting octahydro compounds by either sulfur or selenium, as the final step, and in both cases obtained a dimethylphenanthrene whose properties agreed with the 1,4- compound of Akin, Stamatoff, and Bogert, and without any evidence of the migration of one of the *p*-xylene methyl groups under the conditions of our experiments. Our suggested explanation of Bardhan and Sengupta's results, therefore, is not supported by this evidence.

These two syntheses were as shown in the chart.

Experimental

beta-(*p*-Xylyl)-ethanol, was prepared from bromo-*p*-xylene and ethylene oxide by the Grignard reaction, following the method described by Dreger[5] for the synthesis of *n*-hexyl alcohol, in a yield of 61% and a boiling point of 108–111° at 4 mm. On a redistilled sample, the physical constants were: b. p. 105–106° at 3 mm., d^{25}_4 0.9946, n^{25}_D 1.5286, *M*D calcd. 46.30, *M*D obsd. 46.48. Bardhan and Sengupta, who synthesized it in a different way, gave the b. p. as 110–113° at 5 mm.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.39. Found: C, 79.64; H, 9.40.

Phenylurethan.—Small white rosets of thin needles from petroleum ether, m. p. 79–79.5° (corr.).

Anal. Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: N, 5.29.

beta-(*p*-Xylyl)-ethyl bromide (I) was obtained from the above alcohol and hydrobromic acid, according to the

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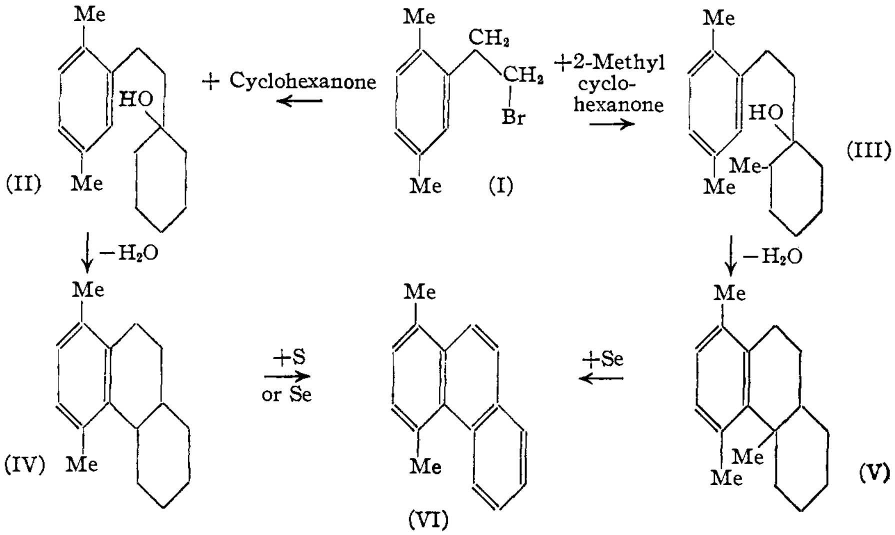
[1] Akin, Stamatoff and Bogert, THIS JOURNAL, **59**, 1268 (1937).

[2] Bardhan and Sengupta, *J. Chem. Soc.*, 2520 (1932).

[3] Bogert and Stamatoff, *Rec. trav. chim.*, **52**, 583 (1933).

[4] Haworth, Mavin, and Sheldrick, *J. Chem. Soc.*, 454 (1934).

(5) Dreger, "Organic Syntheses," Coll. Vol. I, 1932, p. 299.



process recommended by Kamm and Marvel[6] for the preparation of *n*-octyl bromide; b. p. 107–111° at 6 mm.; yield 81%. The physical constants of a redistilled sample were: b. p. 105–106° at 4 mm., d^{25}_{4} 1.2802, n^{25}_{D} 1.5480, M_D calcd. 52.54, M_D obsd. 52.84. Bardhan and Sengupta, whose method of synthesis was not the same as ours, found a b. p. of 104–106° at 5 mm.

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.33; H, 6.15. Found: C, 56.54; H, 6.05.

1-beta-(*p*-Xylylethyl)-cyclohexanol-1 (II), from the bromide (I) and cyclohexanone, *via* the Grignard reaction, was obtained in a yield of 54% and a b. p. of 160–165° at 3–4 mm., for the crude product. Redistilled, its constants were: b. p. 160–162° at 3 mm., d^{25}_{4} 0.9994, n^{25}_{D} 1.5288, M_D calcd. 71.81, M_D obsd. 71.58.

Anal. Calcd. for $C_{16}H_{24}O$: C, 82.76; H, 10.43. Found: C, 83.17; H, 10.29.

Phenylurethan.—Tufts of white needles, from methanol; m. p. 85–86° (corr.).

Anal. Calcd. for $C_{23}H_{29}O_2N$: N, 3.99. Found: N, 4.02.

1-beta-(*p*-Xylylethyl)-2-methylcyclohexanol-1 (III), prepared similarly from the bromide (I) and *o*-methylcyclohexanone, boiled crude at 164–168° at 4 mm.; yield, 58%. The constants of a redistilled sample were: b. p. 159–161° at 2 mm., d^{25}_{4} 1.0008, n^{25}_{D} 1.5297, M_D calcd. 76.43, M_D obsd. 76.04.

Anal. Calcd. for $C_{17}H_{26}O$: C, 82.86, H, 10.64. Found: C, 83.27; H, 10.55.

Phenylurethan.—Small thin white needles from petroleum ether, m. p. 144–145° (corr.).

Anal. Calcd. for $C_{24}H_{31}O_2N$: N, 3.81. Found: N, 3.92.

1,4-Dimethyl-5,6,7,8,9,10,13,14-octahydrophenanthrene (IV).—When dehydrated by the action of phosphorus pentoxide, the *p*-xylylethyl-cyclohexanol (II) gave an 82% yield of hydrocarbon, b. p. 150–154° at 8 mm. On redistillation, a product was obtained with the following constants: b. p. 154–156° at 6 mm., n^{25}_{D} 1.5498.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 90.04; H, 10.69.

During the rectification of the crude product, there were indications of the presence of small amounts of another substance, presumably the spirane to be expected as a by-product, but the quantity of material available was insufficient for its separation or identification.

1,4,13-Trimethyl-5,6,7,8,9,10,13,14-octahydrophenanthrene (V), prepared similarly, from the methylcyclohexanol (III), in a yield of 86% for the crude product (b. p. 160–163° at 6 mm.), possessed the following constants when redistilled: b. p. 155–156° at 4 mm., d^{25}_{4} 0.9975, n^{25}_{D} 1.5460, M_D calcd. 72.69, M_D obsd. 72.37.

Anal. Calcd. for $C_{17}H_{24}$: C, 89.39; H, 10.60. Found: C, 89.12; H, 10.80.

In another series of experiments, the octahydro derivative of the trimethylphenanthrene (V) was dehydrogenated by fusion with selenium, varying the proportions of selenium and hydrocarbon, the temperature (310–350°), and the length of heating (twenty-five to forty hours). In every case, the crude hydrocarbon obtained gave a *picrate*, m. p. 140° (corr.), in yields of 40–84%. Mixtures of this picrate with that secured from the dehydrogenation product of the dimethyl compound (IV) likewise melted at 140° (corr.).

Anal. Calcd. for $C_{22}H_{17}O_7N_3$: C, 60.69; H, 3.93. Found: C, 60.75; H, 3.84.

1,4-Dimethylphenanthrene (VI).—A mixture of 3 g. of the crude octahydro derivative (IV), b. p. 154–156° at 6 mm., with 6 g. of selenium, was heated for thirteen hours at 340–350°, the product extracted with hot methanol, the filtered extract heated to boiling and decolorized with Darco. To the hot filtered solution, there was added 3 g. of picric acid, and 2.8 g. of crystalline picrate was obtained. After 3 recrystallizations, this picrate melted at 140–141° (corr.). It was decomposed by boiling with sodium hydroxide solution. The hydrocarbon was extracted with Skelly-solve B, the extract washed with water, to remove all picrate, the solvent evaporated and

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[6] Kamm and Marvel, "Organic Syntheses," Coll. Vol. I, 1932, p. 28.

the hydrocarbon crystallized from methanol. The crystalline solid thus obtained, m. p. 46–47° (corr.), was recrystallized from dilute methanol six times, then the warm diluted methanol solution was chilled in a refrigerator, and fine long white needles separated, m. p. 49.5–50° (corr.). On the same thermometer, the Akin, Stamatoff, and Bogert[1] product melted at 49.5–50.5° (corr.) and a mixture of the two at 49.5–50.5° (corr.).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.15; H, 6.85. Found: (a) C, 92.97; H, 7.03. (b) C, 92.96; H, 6.97.

Analysis (a) was run on the product melting at 46–47° (corr.), (b) on that melting at 49.5–50° (corr.).

The same product resulted when the octahydro derivative (IV) was dehydrogenated by fusion with sulfur instead of selenium.

Picrate.—We have found that the appearance of the crystals and the m. p. of this picrate vary with its method of preparation and the way in which the m. p. is taken.

When slightly less than the calculated amount of picric acid was added to a methanol solution of the hydrocarbon, orange-yellow needles separated, m. p. 143.5° (corr.), which remelted at the same point.

Anal. Calcd. for $C_{22}H_{17}O_7N_3$: C, 60.69[7]; H, 3.93; N, 9.64. Found: C, 60.69; H, 4.07; N, 9.80.

In the presence of a slight excess of picric acid, however, scarlet flat needles of a picrate were obtained, m. p. 140° (corr.), whose composition was approximately identical with that of the form which melted at 143.5° (corr.).

Anal. Calcd. for $C_{22}H_{17}O_7N_3$: N, 9.64. Found: N, 9.85.

The scarlet color apparently was due to a trace of picric acid for, when these crystals were dissolved in methanol and a very small quantity of 1,4-dimethylphenanthrene was added, the orange-yellow picrate (m. p. 143.5°, corr.) separated.

In Akin, Stamatoff, and Bogert's description[1] of this picrate, they recorded it as crystallizing from methanol in scarlet plates, m. p. 147–148° (corr.); and Akin, in his dissertation,[8] stated that it remelted at 140–144°. But the sample of this picrate left with us by Dr. Akin consisted of orange-yellow needles, melted sharply at 143.5° (corr.) and, when mixed with an equal amount of our own product of the same melting point, caused no change in that figure.

On reviewing the matter with Dr. Akin, he recalled the fact that he too had obtained the picrate in the two forms noted above, but had given the preference to the scarlet crystals as the characteristic form, since the orange-yellow needles were encountered but once, and that for both forms he had observed 147–148° (corr.) as the constant melting point.

Summary

1,4-Dimethylphenanthrene has been prepared by cyclodehydration of both 1-beta-(*p*-xylylethyl)-cyclohexanol-1 and 1-beta-(*p*-xylylethyl)-2-methylcyclohexanol-1, followed by fusion of the resulting octahydro derivatives with sulfur or selenium. The product of both syntheses was a hydrocarbon identical with the 1,4-dimethylphenanthrene of Akin, Stamatoff, and Bogert, and quite different from the compound assigned this constitution by Bardhan and Sengupta.

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(7) Our calculation of the carbon percentage, it will be noted, differs slightly from that given by Akin, Stamatoff, and Bogert, and shows that their analytical result was even closer to the theoretical than indicated.—M. T. B.

(8) Akin, "Dissertation," Columbia University, 1937, p. 31.

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Some Mercury Derivatives of Biphenyl

BY FREDERICK B. HULL

In comparison to the corresponding mercury derivatives of benzene, toluene, and naphthalene, which have been investigated extensively, those of biphenyl have received little attention.

Michaelis[1] prepared *p*-mono- and *p,p'*-dimercuribisbiphenyl and described the halides of the former as melting above 325°. He found it impossible to prepare *p,p'*-biphenyl dimercuric chloride from the corresponding mercuribis compound. Using the method of Nesmejanow,[2] by diazotizing benzidine, precipitating the double salt with mercuric chloride and then treating with copper powder, the preparation was found to be not difficult. This method was also found convenient for the preparation of para and ortho biphenyl mercuric chlorides from which the other derivatives were obtained.

Preliminary experiments in the direct mercuration of biphenyl with one equivalent of mercuric acetate seemed to indicate that the products consisted of a mixture containing a large proportion of bimercurate biphenyl and unreacted biphenyl.

The para and particularly the dipara compounds seem to be characterized by high melting points and insolubility. The ortho compounds have

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(1) Michaelis, *Ber.*, **28**, 592 (1895).

(2) Nesmejanow, *ibid.*, **62B**, 1014 (1929), and "Organic Syntheses," Vol. XII, p. 54.