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.

Some Mercury Derivatives of Biphenyl

BY FREDRICK 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.

lower melting points and greater solubility. In this they show some analogy to the corresponding derivatives of toluene.

p-Biphenyl mercuric nitrate and salicylate have been described and the acetate and hydroxide mentioned in recent patents.[3]

Experimental

***p,p'*-Biphenyl Dimercuric Chloride.**—Using the method of Nesmejanow,[2] from Merck reagent benzidine, the yield of diazonium double salt was 78%. The over-all yield of *p,p'*-biphenyl dimercuric chloride was 32%. It is a nearly white powder, virtually insoluble in boiling benzene, alcohol, and acetone, insoluble in water, and only slightly soluble in hot xylene. It darkens at 230°, shrinks about 275°, starts melting at 286°, considerable is melted at 289°, but not all melts at 335°.

Analysis for chloride. Calcd. for $C_{12}H_8Hg_2Cl_2$: Cl, 11.4. Found: Cl, 11.5.

***p*-Biphenyl Mercuric Chloride.**—This was prepared similarly from Eastman *p*-aminobiphenyl. A 70% yield of the light cream diazonium double salt was obtained. The over-all yield of *p*-biphenyl mercuric chloride was 35%. It is insoluble in water and very slightly soluble in benzene; its solubility in boiling xylene is about 0.2 g. per 100 cc. It darkens slightly at 325° and melts at 328°. Dunker, Starkey, and Jenkins give its melting point as 329°.[4]

***o*-Biphenyl Mercuric Chloride.**—Monsanto *o*-aminobiphenyl was redistilled and diazotized. A 65% yield of the light yellow, slightly soluble diazonium double salt was obtained. Due to the greater reactivity and solubility of the ortho compound, the second step has to be modified somewhat. To avoid explosion, the copper powder is added slowly to the well-stirred suspension of the diazonium double salt in acetone. After the reaction is complete the acetone suspension is filtered, the precipitate extracted with benzene, and the crystals which separate on cooling filtered off. The acetone solution is evaporated and the benzene mother liquors from the first extraction are used for the extraction of the residue. Two more recrystallizations from benzene give pure white, glistening, silky needles, melting sharply at 169.0°. C. Courtot and M.-G. Bastini[5] give the melting point as 165–167°. It is soluble in cold benzene, acetone, and acetic acid, slightly soluble in alcohol, but practically insoluble in water.

By evaporating the brown benzene mother liquor, filtering while hot, and distilling, a considerable quantity of crude *o*-chlorobiphenyl of freezing point 29.2° was recovered.

***o*-Biphenyl Mercuric Acetate.**—The chloride in methanol was boiled with one equivalent of silver acetate. After filtering, the solution was diluted with water, then shaken until the milky liquid crystallized, and the product filtered off. It can be recrystallized conveniently from methanol–water mixtures. It forms pure white needles, m. p. 109.5°. The viscous melt solidifies to a glass which slowly crystallizes. It melts under hot water. It is easily soluble in benzene, alcohol, acetone, and acetic acid and is slightly soluble in water.

***o*-Biphenyl Mercuric Nitrate.**—The chloride was added slowly to boiling methanol containing one equivalent of silver nitrate. After filtering, water was added and the pure white crystals filtered off and washed. The product melts at 156.2° to a pale yellow liquid.

The filtrate was extracted with benzene and then the water solution titrated with sodium hydroxide. According to the equation

$$2C_{12}H_9HgCl + 2AgNO_3 + H_2O \longrightarrow (C_{12}H_9Hg)_2(OH)(NO_3) + HNO_3 + 2AgCl$$

from 1.95 g. of chloride, 0.158 g. of nitric acid should have been liberated. Actually, 0.161 g. was found.

It is soluble in alcohol, benzene, acetone, and slightly soluble in cold water.

***o*-Biphenyl Mercuric Picrate.**—Hot solutions of the acetate and picric acid each in 66% methanol were mixed, cooled, filtered, and the product recrystallized from alcohol and water. It forms bright yellow crystals which start shrinking at 57° and at 99° are orange and appear sintered.

Ortho Mercuribisbiphenyl.—One equivalent of the chloride in alcohol was boiled gently for an hour with three equivalents of sodium cyanide. Needle-like crystals started to separate in ten minutes. The solution was cooled and the crystals filtered off and washed well with alcohol and water and then dried. Diluting the filtrate with water yielded more product. The total yield was 93%. It is insoluble in water; and its solubility in cold alcohol is about 0.06 g. per 100 cc.; it is slightly soluble in benzene and acetone. Its melting point is 168.0°. It resolidifies on cooling and remelts at the same temperature. A 50–50 mixture with the chloride melts from 142 to 150°.

Ortho-mercuribisbiphenyl is a very reactive substance and furnishes a convenient intermediate in the preparation of salts, as the following work illustrates.

***o*-Biphenyl Mercuric Butyrate.**—Ortho-mercuribisbiphenyl and mercuric butyrate were dissolved with gentle warming for a minute in alcohol. On diluting with water, it separated, like the acetate, first as a milk, which on shaking crystallized as white needles. The yield was practically quantitative, m. p. 91.2°. Its solubility in cold water is about 0.04 g. per 100 cc. It is easily soluble in alcohol, benzene, and acetone.

Summary

The following new mercury compounds of biphenyl have been prepared and their properties described: *p,p'*-biphenyl dimercuric chloride, *o*-mercuribisbiphenyl, and *o*-biphenyl mercuric acetate, nitrate, picrate, and butyrate.

The composition of *o*-biphenyl mercuric basic nitrate was determined.

p-Biphenyl mercuric chloride was prepared by a new method. *o*-Biphenyl mercuric chloride was prepared.

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[3] U. S. Patents 2,040,765 and 2,074,040.

[4] Dunker, Starkey and Jenkins, THIS JOURNAL, **58**, 2309 (1936).

[5] C. Courtot and M.-G. Bastini, *Compt. rend.*, **203**, 197 (1936).