the hydrocarbon and trinitrofluorenone were dissolved in hot benzene. On standing in an ice box overnight, the solution deposited light yellow crystals, apparently the hydrocarbon. After several weeks in the ice box, a number of bright red clusters were present. These were picked out, washed in turn with benzene, acetone, and Skellysolve C, then dried *in vacuo;* m. p. 130.6–131.4°.

Anal. (b) Calcd. for $C_{32}H_{19}O_7N_3$: C, 68.9; H, 3.4; N, 7.5. Found: C, 68.7, 68.7; H, 3.5, 3.6; N, 7.6, 7.6.

4-(1-Methylbenzo[c]phenanthryl)-acetic acid, II.—To a solution of 11.12 g. (0.043 mole) of ketone VII in 150 cc. of dry benzene was added 6.0 g. (0.036 mole) of ethyl bromoacetate, 2.4 g. (0.036 mole) of granular zinc and a pinch of iodine. After fifteen minutes of refluxing, the reaction began. Five more like quantities of ester, zinc and iodine were added at half-hour intervals, during which time refluxing was maintained by external heating. Following hydrolysis with dilute hydrochloric acid, the benzene layer was separated and the aqueous layer washed twice with benzene. The combined benzene extracts were evaporated, the residual oil heated ten minutes at 190–200° to effect dehydration, and then distilled *in vacuo*. The distillate was saponified and the resulting product worked up to give a neutral fraction of 1.60 g. (14%) of recovered ketone and an acid fraction which was esterified with methanol–hydrogen chloride, yielding 8.57 g. (63%) of distilled ester.

A mixture of 7.08 g. (0.022 mole) of the above ester and 0.71 g. (0.022 mole) of sulfur was heated for one and one-half hours at 220°, then distilled *in vacuo*. The distillate was saponified, the acid fraction dissolved in acetone and passed through a column of charcoal (Norite A). There was obtained 3.86 g. (57%) of acid II melting above 208°. An analytical sample, colorless prisms from benzene-acetone, melted at 210.1–210.6°.

Anal. (b) Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.4; neut. equiv., 300. Found: C, 83.7, 83.8; H, 5.3, 5.5; neut. equiv., 297, 300.

The amide of II, recrystallized from benzene–acetone, melted at 234.5–235.5° uncor.

Anal. (b) Calcd. for $C_{21}H_{17}ON$: C, 84.3; H, 5.7; N, 4.7. Found: C, 84.4, 84.4; H, 6.1, 5.9; N, 4.7, 4.7.

Resolution of II.—A solution of the chloride of acid II, prepared by treatment of 1.54 g. (0.0041 mole) of II with thionyl chloride and pyridine, in 50 cc. of dry benzene was added dropwise to a well-stirred ice-cold solution of 0.80 g. (0.0051 mole) of *l*-menthol ($[\alpha]_D$ −49.8°, *c*, 2 in absolute ethanol) in 25 cc. of dry benzene. After being stirred for an hour, during which time it came to room temperature, the reaction mixture was hydrolyzed. The benzene layer was separated, washed in turn with dilute hydrochloric acid, water, saturated sodium bicarbonate solution and then dried. Evaporation of the benzene under reduced pressure left an orange oil, which gave 0.39 g. of crystalline material on trituration with Skellysolve F. This material, after five recrystallizations from chloroform–Skellysolve F, melted at 185.5–187.0° and showed a specific rotation of +1.4 ± 0.2° (*c*, 1 in chloroform). Although it was at first believed that this material was the *l*-menthyl ester of II, the analysis indicated that it was impure.

Anal. (b) Calcd. for $C_{31}H_{34}O_2$ (ester): C, 84.9; H, 7.8. Calcd. for $C_{21}H_{16}O_2$ (acid): C, 84.0; H, 5.4. Found: C, 84.9, 84.9; H, 5.4, 5.4.

The five-times recrystallized material was shaken with alcoholic potassium hydroxide for ten minutes, the mixture then diluted with a large quantity of water and extracted repeatedly with ether. Acidification of the aqueous layer precipitated the acid, which was extracted with ether. Evaporation of the ether from the combined extracts left light tan crystals of acid II, m. p. 208.8–209.6°, alone and when mixed with an authentic sample of II. A solution of 0.1053 g. of this acid in 5 cc. of acetone gave an observed rotation of +0.09 ± 0.02°; $[\alpha]^{25}_D$ +2.1 ± 0.4°. No rotation could be observed the following day. Two other resolutions were carried out in the manner described above, giving samples of acid with specific rotations of +1.6 and +1.0°. The acetone solutions of both of these samples displayed no optical activity after standing for twelve hours at room temperature.

Summary

The synthesis of 1-methylbenzo[c]phenanthrene is described. This synthesis completes the series of methylbenzo[c]phenanthrenes, as the other five isomers have been previously described.

The synthesis of 4-(1-methylbenzo[c]phenanthryl)-acetic acid is described, and the dextrorotatory form of this acid has been isolated. The isolation of this optically active acid provides another instance of optical activity of the 4,5-phenanthrene type.

Columbus 10, Ohio Received February 12, 1948

[Contribution from the Central Research Laboratories, Monsanto Chemical Company]

Vinyl Aromatic Compounds. V. Ortho-, Meta- and Para-Isopropenylbiphenyls[1]

By David T. Mowry, Joachim Dazzi, Mary Renoll[2] and Robert W. Shortridge[3]

In a preceding paper[4] the synthesis of ortho-, meta- and para-vinylbiphenyls from the corresponding xenylmethylcarbinols has been described. The present work deals with the preparation of the corresponding isopropenyl derivatives of biphenyl.

In general, the methods employed resembled those used in the earlier work. *o*-Aminobiphenyl was converted to *o*-iodobiphenyl, which by means of its Grignard reagent with acetone gave dimethyl-*o*-xenylcarbinol. This was dehydrated catalytically in the vapor phase over alumina to give *o*-isopropenylbiphenyl in 83% yield. It is interesting to note that under these conditions the reaction takes a different course from that reported by Anchel and Blatt[5] who dehydrated the same carbinol in the liquid phase with sulfuric acid or a mixture of acetic acid and hydrogen chloride to give nearly quantitative yields of 9,9-

---

[1] Preceding paper in this series, This Journal, **69**, 851 (1947).

[2] Present address: Department of Chemistry, The Ohio State University, Columbus, Ohio.

[3] Present address: Midwest Research Institute, Kansas City, Missouri.

[4] Huber, Renoll, Rossow and Mowry, This Journal, **68**, 1109 (1946).

[5] Anchel and Blatt, *ibid.*, **63**, 1948–1952 (1941).

dimethylfluorene. No dimethylfluorene was detected in the product from the vapor phase dehydration, although it is possible that minor amounts may have been formed.

p-Acetylbiphenyl was treated with methylmagnesium bromide to give a 78–85% yield of dimethyl-*p*-xenylcarbinol. This was dehydrated in a similar fashion to *p*-isopropenylbiphenyl.

m-Bromobiphenyl was prepared in four steps from *o*-aminobiphenyl as previously described.[4] The Grignard reagent from the bromide was treated with acetone to give crude dimethyl-*m*-xenylcarbinol which could not be distilled without decomposition and could not be induced to crystallize. This behavior was to be expected since several previously described meta derivatives of biphenyl are reported to freeze to non-crystalline glasses on cooling.[4] Consequently the crude material was dehydrated by refluxing with acetic anhydride to give *m*-isopropenylbiphenyl in 57% yield based on the *m*-bromobiphenyl.

Experimental

Dimethyl-*o*-xenylcarbinol.—*o*-Iodobiphenyl was prepared in 83% yield from *o*-aminobiphenyl by the Sandmeyer method according to the procedure of Gilman, Kirby and Kenney.[6] Four hundred sixty-seven grams of this product, b. p. 145–147° (6 mm.), was converted to the Grignard reagent, using 44 g. of magnesium in 750 cc. of anhydrous ether. The solution was cooled to 5° and 97 g. of dry acetone in 100 cc. of ether was added with stirring during ninety minutes, keeping the temperature below 20°. After standing overnight, a solution of 250 g. of ammonium chloride in 1200 cc. of water was added and the ether layer separated and evaporated. The crystalline residue was recrystallized twice from hexane to give 122 g. (34%) of fluffy needles, m. p. 69.5–70.5°; mixed melting point with biphenyl, 46–48°. Anchel and Blatt[5] report m. p. 73° for a sample prepared from the methyl Grignard reagent and methyl *o*-phenylbenzoate.

***o*-Isopropenylbiphenyl.**—A solution of 231 g. of dimethyl-*o*-xenylcarbinol in 275 cc. of dioxane was passed over activated alumina at 275° and 90–100 mm. pressure using the technique and apparatus that has been described previously.[7] Two distillations gave 176.5 g. (83%) of *o*-isopropenylbiphenyl, b. p. 107–109° (2 mm.), $n^{25}D$ 1.5925 which freezes to a glass at about −40°. A bromide-bromate analysis[8] indicated that the material was 98.5% pure.

Anal.[9] Calcd. for $C_{15}H_{14}$: C, 92.73; H, 7.26. Found: C, 92.59; H, 7.29.

Dimethyl-*p*-xenylcarbinol.—An ethereal solution of the Grignard reagent prepared in the usual manner from 48.6 g. of magnesium (2.0 moles) and methyl bromide was treated with 371 g. (1.84 moles) of *p*-acetylbiphenyl dissolved in 1.5 l. of benzene during the course of one hour. After standing overnight the material was hydrolyzed with dilute sulfuric acid. The organic layer was separated, washed with water and evaporated to give 330 g. (85%) of crude dimethyl-*p*-xenylcarbinol. Another similar run gave a 78% yield. The material after recrystallization from a mixture of benzene and hexane melted at 92–93°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 85.22; H, 7.62.

***p*-Isopropenylbiphenyl.**—A 30% solution of dimethyl-*p*-xenylcarbinol in dioxane was dehydrated in a manner similar to that described for the ortho isomer. A 79–84% yield of the hydrocarbon, b. p. 122–124° (1 mm.) was obtained. After recrystallization from dilute ethanol, the material melted at 119.0–119.5°. When mixed with a sample of *p*-vinylbiphenyl[4] (m. p. 120°) the melting point was markedly depressed. The material showed 100.1% unsaturation by the bromide-bromate titration.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.72; H, 7.26. Found: C, 92.60; H, 7.25.

***m*-Isopropenylbiphenyl.**—*m*-Bromobiphenyl was prepared from *o*-aminobiphenyl in 62% over-all yield by the four-step synthesis previously described.[1] The improvement in yield (51% was formerly reported) was due to a modification in the deamination step where the crude *m*-bromobiphenyl resulting from decomposition of the diazonium solution was extracted with benzene and washed free of sulfuric acid before distillation. The Grignard reagent was prepared from 150 g. of the bromide (0.64 mole) in the usual fashion and treated with a 20% excess of dry acetone in ether. After standing overnight, the material was hydrolyzed with dilute hydrochloric acid, separated, washed with water and evaporated to give 124 g. (92%) of crude oily dimethyl-*m*-xenylcarbinol which could not be purified by crystallization or distillation.

Two hundred forty-three grams of this crude product was refluxed with an excess (280 g.) of acetic anhydride for three hours. The acetic acid and excess anhydride were removed under vacuum and the product fractionated to give 29 g. of biphenyl and 141 g. of *m*-isopropenylbiphenyl, b. p. 160–161° (12 mm.); $n^{25}D$ 1.6128. A bromide-bromate titration indicated a purity of 99.6%.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.72; H, 7.26. Found: C, 92.23; H, 7.50.

Summary

Ortho-, meta- and para-isopropenylbiphenyl have been synthesized by dehydration of the appropriate dimethylxenylcarbinols.

DAYTON, OHIO RECEIVED JANUARY 23, 1948

---

(6) Gilman, Kirby and Kenney, THIS JOURNAL, **52**, 2252 (1929).

(7) Mowry, Renoll and Huber, *ibid.*, **68**, 1105 (1946).

(8) Mulliken and Wakeman, *Ind. Eng. Chem., Anal. Ed.*, **7**, 59 (1935).

[9] Ultimate analyses by the Oakwold Laboratories, Alexandria, Virginia.