water (3 cc.) was refluxed with zinc (20 mesh) for three hours. The nitro compound slowly dissolved and at the end a clear solution resulted. This was poured over ice and the white precipitate was removed and crystallized twice from ethanol. The product (150 mg.) formed pink needles which melted at 189–190° to a dark reddish liquid. The material was not analytically pure, however.

Anal. Calcd. for $C_{25}H_{21}N$: C, 90.53; H, 5.70. Found: C, 89.53; H, 5.99.

Summary

1. The first step in the reaction between lithium and diphenylacetylene is the formation of 1,2,3,4-tetraphenyl-1,4-dilithiumbutadiene-1,3.

2. The compound resulting from alcoholysis of the first lithium derivative is 1,2,3,4-tetraphenylbutadiene, and not 1-benzal-2,3-diphenylhydrindene as has been previously reported.

3. The relative amounts of metal and hydrocarbon determine the nature of the final product formed whenl ithium reacts with diphenylacetylene. When the molar ratio of hydrocarbon and metal is 1:1, the final product is the tetraphenylbutadiene. When excess metal is used, the final product is a hydrocarbon which appears to be 1,2,3-triphenylnaphthalene.

4. Carbonation of the metallic derivative which corresponds to 1,2,3-triphenylnaphthalene leads to a substance previously reported as a monocarboxy derivative of this hydrocarbon, and having this composition. Yet this substance shows surprising properties for an acid, for it is not soluble in sodium carbonate, sodium hydroxide or Claisen alkali.

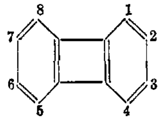
MINNEAPOLIS, MINNESOTA RECEIVED JANUARY 2, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

Biphenylene

BY WARREN C. LOTHROP

The history of the interesting hydrocarbon biphenylene (I)[1] is a series of repeated failures in its preparation and of only one isolated and irreproducible success. The earliest report is that of Hosaeus,[2] who carried out a Wurtz reaction with *o*-dibromobenzene but obtained biphenyl as the only hydrocarbon. An internal Ullmann reaction[3] in which 2,2′-diaminobiphenyl was diazotized and treated with copper, gave carbazole, while attempted dehydration of 2-hydroxybiphenyl not unexpectedly also failed.[4]



I

Dobbie, Fox and Gauge[5] in a series of articles claimed the preparation of the hydrocarbon in 100% yield by the intramolecular Wurtz reaction of freshly cut sodium on 2,2′-dibromobiphenyl. They reported analyses of a compound very similar to biphenyl and based their proof on its method of synthesis and its oxidation in part to phthalic acid. In their last paper they reported failure to obtain anything but resins from a corresponding reaction on 2,2′-diiodobiphenyl but did describe several reactions of their new hydrocarbon. These indicated a strained central ring, since bromine opened it to give the starting material, 2,2′-dibromobiphenyl, while dilute nitric acid formed dibenzofuran among other products.

Nierenstein[6] at this time found that a zinc dust distillation of purpurotannin gave a hydrocarbon identical with that of Dobbie, Fox and Gauge. This seemed strange, since to purpurotannin was ascribed a substituted dibenzofuran structure while Hoffmeister[7] had found that dibenzofuran itself did not yield biphenylene on such treatment.

Attempts by other workers[8] to repeat the original preparation of the compound from 2,2′-dibromobiphenyl[5] failed completely, so that doubts of the possible existence of a compound containing a cyclobutadiene ring could be rea-

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[1] The nomenclature is that of *Chemical Abstracts*, Third Decennial Index, p. 3730, but the numbering in the diagram is suggested as more comparable to that used in other hydrocarbons.

[2] Hosaeus, *Monatsh.*, **14**, 323 (1893).

[3] Niementowski, *Ber.*, **34**, 3331 (1901).

[4] Cullinane, Morgan and Plummer, *Rec. trav. chim.*, **56**, 627 (1937).

[5] Dobbie, Fox and Gauge, *J. Chem. Soc.*, **99**, 683, 1615 (1911); **103**, 36 (1913).

[6] Nierenstein, *Ann.*, **386**, 318 (1911); "The Natural Organic Tannins," Churchill, 1934.

[7] Hoffmeister, *Ann.*, **159**, 213 (1871).

[8] (a) Mascarelli and Gatti, *Gazz. chim. ital.*, **63**, 661 (1933); (b) Mascarelli, Gatti and Longo, *ibid.*, **63**, 654 (1933); (c) Schwechten, *Ber.*, **65**, 1605 (1932).

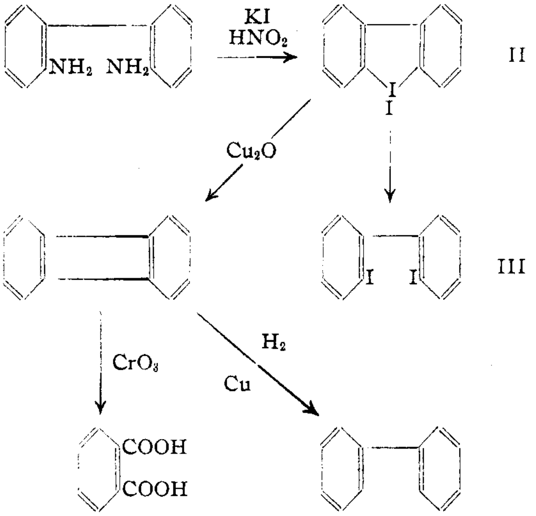
sonably expressed[9] although a case of such a compound has been reported[10]: namely, 2,3-binaphthylene.

Because an investigation of biphenylene might contribute to the theory of aromatic chemistry as a whole, supplying in its central ring a possible cyclobutadiene system and at the same time affording an extreme case of the Mills–Nixon effect,[11] it was thought worth while to re-investigate its preparation.

Attempts to eliminate the bromine atoms from 2,2′-dibromobiphenyl by the action of hydrogen, lithium, sodium and potassium were all successful, but the product in each case was biphenyl obtained generally in very poor yield and contaminated with a bromine containing oil which was taken to be 2-bromobiphenyl. Calcium and zinc were without effect and magnesium as expected[12] reacted only with difficulty with the bromine in the 2-position and could not be forced to replace the second bromine at 2′ even under the most drastic conditions. In fact the great stability of 2,2′-dibromobiphenyl under very severe treatment is noteworthy.

Pure copper metal likewise was without effect, but some old copper powder which had been partially oxidized by long standing gave a small quantity of a new hydrocarbon which was readily volatile with steam, crystallized from alcohol in long straw-colored prisms melting at 109–110°, and formed a scarlet picrate melting at 121–122°. Subsequent experiments showed that neither copper nor cupric oxide had acted upon the dibromide but that cuprous oxide alone was the active reagent.

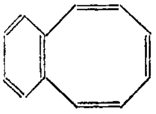
Some unchanged dibromide was always present in the crude product and tedious to remove since it necessitated the isolation of the hydrocarbon as its picrate. To avoid this difficulty, the biphenylene iodonium iodide (II) previously reported[13] was prepared and pyrolyzed directly with cuprous oxide. Very little 2,2′-diiodobiphenyl (III) appeared in the product and the yields of the hydrocarbon were much improved, although very poor even then, so that from 223 g. of *o*-chloronitrobenzene only 3.4 g. of pure product resulted:



Molecular weight determinations in benzene and camphor agreed with the formula for biphenylene rather than for such dimolecular coupling possibilities as 1,2,6,7-dibenzpyrene,[14] 2,2′-diphenylbiphenyl[15] or tetrabenzocycloöctatetraene. The first two being known may be excluded on other grounds as well.

Analyses of the hydrocarbon and its picrate, the formation of which is significant, agreed with the formula $C_{12}H_8$, but more convincing proof was the ready oxidation of the substance to phthalic acid by the action of chromic oxide, thereby establishing the presence of ortho substitution. Furthermore when the compound was passed over red hot copper in an atmosphere of hydrogen, conditions which will remove the bromine atoms from 2,2′-dibromobiphenyl, another hydrocarbon resulted which after three recrystallizations melted at 66° and mixed with biphenyl (m. p. 69–70°) gave a melting point of 68–69°. This evidence while somewhat inconclusive due to the small quantities at hand and the difficulty of separating the two hydrocarbons completely by crystallization, is compatible only with biphenylene.

The remote possibility of some deep seated change in which one of the benzene rings of biphenyl has been opened, yielding perhaps IV



IV

cannot be rigorously excluded now although it seems unlikely.

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[9] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 19.

[10] Rosenhauer, Braun, Pummerer and Riegelbauer, *Ber.*, **70**, 2284 (1937).

[11] Lothrop, THIS JOURNAL, **62**, 132 (1940); Long and Fieser, *ibid.*, **62**, 2670 (1940).

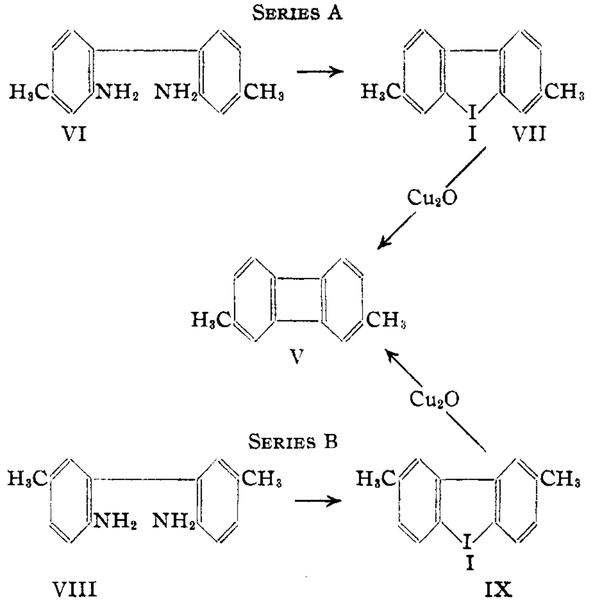
[12] Case, *ibid.*, **58**, 1246 (1936).

[13] Mascarelli and Benati, *Gazz. chim. ital.*, **38**, 627 (1908).

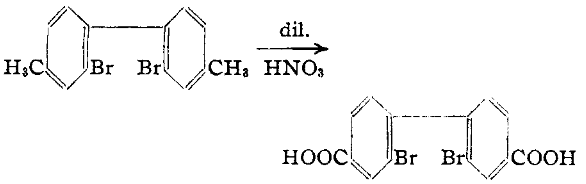
[14] Sako, *Bull. Soc. Chem. Japan*, **9**, 55 (1934).

[15] Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927).

In order to see whether the dehalogenation reaction used to prepare biphenylene could be considered general, it seemed desirable to investigate several similar cases. The first of these may now be reported: the preparation of 2,7-dimethylbiphenylene (V). This compound could theoretically be prepared by two different routes thus offering an easy test of the structural formula of biphenylene. The first route (Series A) would involve the preparation of 2,7-dimethylbiphenylene iodonium iodide (VII) and the second route (Series B) the preparation of 3,6-dimethylbiphenylene iodonium iodide (IX). Both of these substances should yield the same product in the final step



In carrying through Series A no compounds not previously reported were encountered; however, a discrepancy was observed between the properties of 2,2′-dibromo-*p*,*p*′-bitolyl as prepared from the corresponding diamine and those recorded by Marler and Turner[16] for a material not analyzed by them. The identity of the questioned compound was established by analysis and oxidation to the corresponding known[17] dicarboxylic acid X



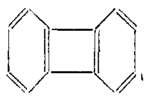
X

We are indebted to Dr. Roger Adams for a sample of this acid for comparison.

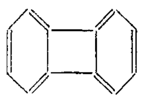
When either the above-mentioned dibromide or iodonium iodide (VII) was heated with cuprous oxide a steam volatile hydrocarbon was obtained which crystallized from alcohol in pearly, yellow plates (m. p. 112–113°), the color persisting after several crystallizations while the melting point remained constant. When the compound was treated in alcoholic solution with picric acid a picrate crystallized out in long deep crimson needles (m. p. 110°). Analyses of the compound and molecular weight determinations agreed with the formula $C_{14}H_{12}$, and the compound was taken to be 2,7-dimethylbiphenylene (V).

Series B presented considerable trouble due to the difficulty in obtaining a sufficient quantity of the starting material 3-amino-4-nitrotoluene. Once this was prepared, the series of reactions was performed with complete success, yielding a final product identical in all respects with the hydrocarbon obtained by Series A.

The complete agreement found between prediction and experiment adds considerable weight in support of the formulas as written for these new hydrocarbons and suggests either that the cyclobutadiene ring may not be too strained to exist if fused with two benzene rings (XI), or that the Mills–Nixon effect may operate to stabilize the molecule in a less strained cyclobutane form (XII)



XI



XII

or that the coplanar molecule has considerable resonance energy. Furthermore, the formation of such stable and highly colored picrates would seem to confirm a fused system of three rings.[18]

Experimental Part

2,2′-Diaminobiphenyl was obtained from 2,2′-dinitrobiphenyl ("Organic Syntheses," Vol. 20, p. 45) as previously described[19] by reduction with tin and hydrochloric acid. The recovery of the free amine from the alkaline mixture was complicated by the formation of thick emulsions with ether, which were separated by centrifuging.

2,2′-Dibromobiphenyl was prepared without difficulty following the procedure of Schwechten.[8c] A perfectly white product could be obtained only after distillation at atmospheric pressure (m. p. 80–81°).

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[16] Marler and Turner, *J. Chem. Soc.*, 266 (1937).

[17] Searle and Adams, THIS JOURNAL, **56**, 2112 (1934).

[18] *Cf.* Baril and Hauber, *ibid.*, **53**, 1090 (1931).

[19] Macrae and Tucker, *J. Chem. Soc.*, 1520 (1933).

Dehalogenation of 2,2′-Dibromobiphenyl

By Hydrogen.—When 0.80 g. of the dibromide was passed in the vapor state through red hot copper gauze in a slow current of hydrogen, 0.12 g. of material crystallizing from alcohol in large plates (m. p. 68–69°) was obtained. It did not depress the melting point of biphenyl.

Replacement of hydrogen by carbon dioxide resulted in extensive decomposition; replacement by nitrogen gave no reaction.

By Alkali Metals.—When 2.0-g. samples of the dibromide were refluxed with or without solvent with molecular quantities or with excess of lithium, sodium or potassium, the results were identical. In all cases biphenyl (0.10 g. to 0.52 g.) was obtained together with a yellow resin and varying amounts of a dense halogen-containing oil (2-bromobiphenyl?). When magnesium was used, one mole only reacted and the sole product was the same dense oil.

By Calcium, Aluminum, Zinc, Copper or Cupric Oxides.—In all these cases refluxing of the dibromide with the reagent with or without solvent gave no reaction, the material being recovered unchanged.

By Cuprous Oxide.—An intimate mixture of 10.0 g. of the dibromide and 150 g. of Baker C. P. cuprous oxide was heated in a Pyrex retort until distillation ceased. The yellow semi-crystalline distillate was steam distilled, and then fractionally crystallized from a saturated alcoholic solution of picric acid. The deep red solution deposited fine scarlet needles which were recrystallized from alcohol, yielding 0.48 g. of pure picrate (m. p. 122°).

Anal. Calcd. for $C_{12}H_8 \cdot C_6H_3O_7N_3$: N, 11.02. Found: N, 11.04.

The picrate, heated overnight at 100° on a watch glass covered with a funnel, decomposed, giving a white crystalline sublimate on the funnel and depositing picric acid on the watch glass. The sublimate crystallized beautifully from alcohol in straw-colored elongated prisms (m. p. 110°). They weighed 0.15 g. which represents a 5% yield, considering that 3.95 g. of unreacted dibromide was recovered from the picrate mother liquors. Further crystallization failed to remove the color or raise the melting point. The hydrocarbon was somewhat volatile and had an odor resembling biphenyl.

Anal. Calcd. for $C_{12}H_8$: C, 94.59; H, 5.31; mol. wt., 152. Found: C, 94.70, 94.72; H, 5.57, 5.76; mol. wt., 150 (Rast micro), 145 (boiling benzene macro).

Biphenylene Iodonium Iodide (II).—Using a procedure described by Searle and Adams[20] for a similar compound, gave higher yields than those reported by Mascarelli and Benati.[13] To a solution of 47.5 g. of 2,2′-diaminobiphenyl in 260 cc. of concentrated hydrochloric acid and 260 cc. of water at 5°, a solution of 37 g. of sodium nitrite in 125 cc. of water was added slowly with mechanical stirring. Stirring was continued for fifteen minutes and then a solution of 130 g. of potassium iodide in 250 cc. of ice water was poured in slowly with manual stirring. A thick black paste separated at once. The mixture was allowed to stand at room temperature for three hours and then with excess of sodium bisulfite overnight. The yellow-green solid which remained was filtered off, washed well with bisulfite solution and water and then with cold methanol. The latter removed 5.0 g. of 2,2′-diiodobiphenyl (III) (m. p. 106–108°) which proved to be identical with the product obtained by pyrolysis of the iodonium iodide.[21]

The yield of the partially purified iodonium iodide (m. p. 205–210° dec.) was 58.5 g. or 56%. The salt was suitable for use in the dehalogenation reaction without any further treatment.

Pyrolysis of Biphenylene Iodonium Iodide with Cuprous Oxide was conducted in a manner similar to that described above in the case of the dibromide. It was found convenient to run several batches at once and possible to use the same cuprous oxide three times before its efficiency was noticeably impaired.

When 58.5 g. of the iodonium iodide was thus treated, 10.0 g. of a sludge of crystals and oil was obtained in the steam distillate. This was crystallized from alcohol, 3.2 g. of the hydrocarbon (m. p. 109–110°) being obtained at once, and from the mother liquors 0.2 g. more. Further concentration of the mother liquors gave 0.1 g. of carbazole (m. p. 238–239°) which was confirmed by a mixed melting point determination. The remainder was 6.2 g. of a mobile yellow oil which was evidently 2-iodobiphenyl.

The yellow, resinous material non-volatile with steam was found to contain considerable phenazone (m. p. 153–154°)[22] readily isolated as its picrate (3.5 g.) (m. p. 190–191°) which is very insoluble in acetone. There was also obtained 0.35 g. of a picrate, forming brilliant orange-red needles (m. p. 175–178°) on recrystallization from alcohol. It was not further investigated.

Oxidation of the hydrocarbon was accomplished by the action of excess chromic oxide in acid solution at room temperature. An acid resulted, crystallizing from dilute sulfuric acid in colorless needles melting at 185° with loss of water and remelting at 127° with sublimation—properties of phthalic acid. Further proof of identity was afforded by the formation of the characteristic anil of phthalic acid (m. p. 203–204° with sublimation) and mixed melting point determinations.

Phthalic acid also resulted from the refluxing of the hydrocarbon with dilute nitric acid.

Reduction of the Hydrocarbon.—When 50 mg. of the hydrocarbon was passed over hot copper in a stream of hydrogen, about a third of the material was converted into a substance crystallizing from alcohol in pearly plates (m. p. 66°). These mixed with biphenyl (m. p. 69–70°) melted at 68–69°. The remainder of the material was unchanged (m. p. 110°).

Series A

2,2′-Dinitro-*p,p′*-bitolyl was prepared from commercial 4-amino-3-nitrotoluene as described by Niementowski.[8] Reduction with tin and hydrochloric acid gave **2,2′-diamino-*p,p′*-bitolyl**[3] in 50% yield. The chief losses were mechanical due to the formation of thick emulsions of the basic reaction mixture with extracting solvents.

2,2′-Dibromo-*p,p′*-bitolyl was obtained in 54% yield by an adaptation of Schwechten's method.[8c] The product was only slightly volatile with steam and melted at 74–75°

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[20] Searle and Adams, THIS JOURNAL, **55**, 1649 (1933).

[21] For an investigation of the mechanism of this type of reaction see: Lucas, Kennedy and Wilmot, *ibid.*, **58**, 157 (1936).

[22] Sandin and Cairns, *ibid.*, **58**, 2019 (1936), give m. p.'s of 155° and 191° for phenazone and its picrate.

while Marler and Turner[16] state that the dibromide is steam-volatile and melts at 114–115°.

Anal. Calcd. for $C_{14}H_{12}Br_2$: C, 49.47; H, 3.56; Br, 47.0. Found: C, 49.83; H, 3.76; Br, 47.0.

A sample (1.0 g.) of the dibromide refluxed with 30 cc. of concentrated nitric acid and 20 cc. of water for five days, gave a white solid which after sublimation and crystallization from alcohol yielded a pure acid (m. p. 307–309° cor.). Neutralization equivalent calcd. for $C_{14}H_8O_4Br_2$: 202. Found: 199.

A mixture with a sample of 2,2′-dibromo-4,4′-dicarboxylbiphenyl (X)[17] failed to depress the melting point of either constituent and melted at 308–309°, thus proving the structure of the dibromide. Several attempts to prepare some of the compound by the Sandmeyer reaction as mentioned by Marler and Turner[16] failed entirely, yielding only 2,7-dimethylcarbazole.[3]

2,7-Dimethylbiphenylene Iodonium Iodide[16] (VII).—This salt was prepared using exactly the same procedure as described for the preparation of biphenylene iodonium iodide. The yield from 25 g. of the diamine was 21 g. of brownish-yellow salt (m. p. 200–202° dec.), which is 41% of the theoretical.

2,2′-Diiodo-*p,p′*-bitolyl[16] was obtained on pyrolysis of the iodonium iodide as white prisms from methanol (m. p. 111–113°). It was also found in small amounts in the product of the pyrolysis with cuprous oxide (see below).

2,7-Dimethylbiphenylene (V).—When 21 g. of VII was treated as described previously in the preparation of biphenylene, a yellow steam-volatile sludge of crystals resulted which after three crystallizations from alcohol appeared as yellow plates (m. p. 112°) having an odor reminiscent of naphthalene and fluorene. Purification of the hydrocarbon through its recrystallized picrate did not remove the color or change the melting point. The yield was 0.38 g., 4.5%.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.28; H, 6.71; mol. wt., 180. Found: C, 93.20, 93.13; H, 7.25, 7.31; mol. wt., 182 (Rast micro).

From the mother liquors of the crystallizations two picrates were isolated. The first on recrystallization from alcohol weighed 0.36 g. and formed a mass of dark maroon needles (m. p. 110–111°). This was the picrate of 2,7-dimethylbiphenylene possibly combined with alcohol of crystallization. The compound changed in composition on standing exposed to the air and proved difficult to analyze.

Anal. Calcd. for $C_{14}H_{12} \cdot C_6H_3O_7N_3 \cdot 2C_2H_5OH$: C, 57.49; H, 5.43; N, 8.38. Found: C, 59.36; H, 4.67; N, 8.45.

The second picrate was obtained as sparingly soluble yellow prisms (m. p. 215–217°), evidently the picrate of 2,7-dimethylphenazone,[23] a likely impurity in the iodonium iodide.

Pyrolysis of 2,2′-dibromo-*p,p′*-bitolyl by the same method also gave the same hydrocarbon and picrate but in much poorer yield with considerable bromide distilling over without reacting.

Series B

3,4-Dinitrotoluene was prepared from 4-amino-3-nitrotoluene by a two step oxidation, Page and Heasman's directions[24] being followed with the substitution of concentrated for fuming nitric acid in the second step. Using 100-g. quantities of the amine the average yield was 66 g. of orange crystals (m. p. 60°) or 56% of the theoretical.

3-Amino-4-nitrotoluene was obtained as previously described[25] by the action of ammonia in a methanol solution in an autoclave at 160° for six hours.[26]

6,6′-Dinitro-*m,m′*-bitolyl has been reported previously,[27] but in the present work it was prepared by the Ullmann reaction on 3-amino-4-nitrotoluene using Niementowski's directions[8] for the isomeric compound of Series A. The yield was only 31% which would suggest that the method of Case and Koft is preferable.

Reduction in the usual manner gave **6,6′-diamino-*m,m′*-bitolyl** (VIII) crystallizing from petroleum ether in rosets (m. p. 78–79°).

3,6-Dimethylbiphenylene Iodonium Iodide (IX) was prepared from the above diamine in the usual way. From 10.4 g. of the latter, 5.5 g. of a fine, yellow, powdery salt (m. p. 230° dec.) resulted, a 25% yield.

Anal. Calcd. for $C_{14}H_{12}I_2$: I, 58.5. Found: I, 58.2.

From the methanol extracts a small quantity of white prisms was recovered which after recrystallization from acetic acid or acetone melted at 172°. This **6,6′-diiodo-*m,m′*-bitolyl** also appeared as a by-product (3.3 g.) in the pyrolysis of the iodonium iodide with cuprous oxide (see below).

Anal. Calcd. for $C_{14}H_{12}I_2$: I, 58.5. Found: I, 58.0.

2,7-Dimethylbiphenylene V.—Treatment of 21.5 g. of IX in the customary manner with cuprous oxide yielded 0.57 g. of steam volatile solid which after two crystallizations from alcohol as yellow plates melted at 112°. The product gave a picrate (m. p. 110°) crystallizing from alcohol in deep crimson needles. Mixed m. p. determinations of these two substances with the products of Series A gave no depression.

Summary

The history of biphenylene has been presented and the syntheses of two new hydrocarbons believed to be biphenylene and 2,7-dimethylbiphenylene are described, the latter by two different routes. This together with other evidence supports the suggested biphenylene ring system.

HARTFORD, CONNECTICUT RECEIVED FEBRUARY 7, 1941

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[23] Ullmann and Dieterle, *Ber.*, **37**, 23 (1904).

[24] Page and Heasman, *J. Chem. Soc.*, **123**, 3235 (1923).

[25] Kenner and Parkin, *ibid.*, **117**, 858 (1920); Geerling and Wibaut, *Rec. trav. chim.*, **53**, 1014 (1934); *cf.* Mangini and Colonna, *Gazz. chim. ital.*, **68**, 543 (1938).

[26] We are indebted to Professor L. F. Fieser for his kindness in making available to us the Harvard autoclave.

[27] Täuber and Löwenberg, *Ber.*, **24**, 2597 (1891); Case and Koft, THIS JOURNAL, **63**, 508 (1941).