[CONTRIBUTION FROM THE McPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Condensed Cyclobutane Aromatic Compounds. XII.
Some 5-Substituted Derivatives of Benzo[a]biphenylene

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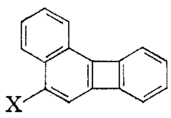
The dehydrohalogenation of *trans*-1,2-diiodobenzocyclobutene afforded 5-iodobenzo[a]biphenylene. The latter iodide served as starting material for the synthesis of the 5-carboxy-, 5-cyano- and 5-acetyl- derivatives of benzo[a]biphenylene.

The only reported substitution product of the hydrocarbon benzo[a]biphenylene (I)[1] is the 5-bromo derivative (II), obtained as the end product of the dehydrobromination[2] of *trans*-1,2-dibromobenzocyclobutene.[3]

As anticipated, the dehydrohalogenation of *trans*-1,2-diiodobenzocyclobutene[3,4] by potassium *t*-butoxide proceeded in a completely analogous manner to give 5-iodobenzo[a]biphenylene (III), m.p. 131–132°, in 71% yield. This readily available iodo compound was employed as the starting material for the synthesis of several other 5-substituted benzo[a]biphenylenes.

5-Iodobenzo[a]biphenylene underwent metal exchange with *n*-butyl lithium. The resulting lithium derivative (IV) was treated with carbon dioxide to give, in 57% yield, benzo[a]biphenylene-5-carboxylic acid (V), m.p. 257°. The same acid was obtained in lower yield, by carbonation of the lithio derivative prepared from the bromide II, as well as by carbonation of the Grignard derivative (VI) of the iodide II. Benzo[a]biphenylene-5-carboxylic acid is scarlet in color as the free acid, although the corresponding anion has the lemon yellow color characteristic of the parent hydrocarbon benzo[a]biphenylene.[2] The acid V was converted *via* the acid chloride (VII), into the orange methyl ester (VIII), m.p. 126–127°, and also into the yellow amide (IX), m.p. 271–272°. Dehydration of the amide with thionyl chloride afforded the orange 5-cyanobenzo[a]biphenylene (X), which was obtained directly from iodide III by reaction with cuprous cyanide.

Treatment of 5-cyanobenzo[a]biphenylene with methylmagnesium iodide gave, after hydrolysis of the intermediate imine, 5-acetylbenzo[a]biphenylene (XI). The bright red ketone XI, m.p. 85–86°, was isolated in pure form only in low yield (11%) after initial separation as a crude 2,4,7-trinitrofluorenone complex. It was prepared, however, in excellent yield (93%) by an alternate synthesis from dimethylcadmium and the acid chloride VII. An attempt was made to effect the direct Friedel-Crafts acetylation of benzo[a]biphenylene under conditions employed successfully for the conversion of biphenylene to 2-acetylbiphenylene.[5] Although partial reaction of the hydrocarbon occurred, none of the 5-acetyl derivative (XI) was found after careful chromatographic examination of the oily reaction mixture.



I. X = H
II. X = Br
III. X = I
IV. X = Li
V. X = COOH
VI. X = MgI
VII. X = COCl
VIII. X = $COOCH_3$
IX. X = $CONH_2$
X. X = CN
XI. X = $COCH_3$

EXPERIMENTAL[6]

5-Iodobenzo[a]*biphenylene* (III). Finely ground *trans*-1,2-diiodobenzocyclobutene[3,4] (2.50 g.) was added slowly to a hot solution of potassium *t*-butoxide prepared by dissolving potassium (1.60 g.) in *t*-butanol (32 ml.). The orange solution was refluxed for 30 min. Water (20 ml.) was then added, followed by sufficient acetic acid to neutralize the excess base. The mixture was cooled and the orange crystalline precipitate (1.00 g.) was filtered, washed with water, and dried. The crude product was purified by continuous extraction with petroleum ether (30–60°) in a Soxhlet apparatus, evaporation of the extract and crystallization from aqueous ethanol to give, in two crops, orange needles of iodide III (0.82 g., 71%). The first crop (0.69 g.), m.p. 131–132°, was of analytical purity.

Anal. Calcd. for $C_{16}H_9I$: C, 58.56; H, 2.76; I, 38.68. Found C, 58.56; H, 2.75; I, 38.55. Ultraviolet spectrum (ethanol): λ_{max} 226 (log ϵ 4.23); λ_{max} 266 (log ϵ 4.31).

Benzo[a]*biphenylene-5-carboxylic acid* (V). *A. By carbonation of Grignard reagent* VI. To an excess of magnesium turnings in dry ether (25 ml.) was added 5-iodobenzo[a]biphenylene (0.100 g.), followed by a few drops of methyl iodide. After refluxing for 30 min., the yellow ether solution was pipetted from the residual magnesium and gaseous carbon dioxide was passed through it slowly for 5 min. Dilute hydrochloric acid was added and the ether solution was shaken with 5% sodium hydroxide until no further color passed into the aqueous phase. The lemon yellow solution of the sodium salt of V was acidified and the orange flocculent precipitate was extracted into ether. Evaporation of the

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[1] M. P. Cava and J. F. Stucker, *J. Am. Chem. Soc.*, **77**, 6022 (1955).

[2] M. P. Cava and J. F. Stucker, *J. Am. Chem. Soc.*, **79**, 1706 (1957).

[3] M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957).

[4] F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958).

[5] W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954).

[6] Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn., and by Schwarzkopf Laboratories, Woodside, N. Y. All melting points are uncorrected.

dried extract and crystallization of the residue from benzene–methanol–petroleum ether (30–60°) mixture afforded small bright red needles of V (0.029 g., 39%), m.p. 257°.

Anal. Calcd. for $C_{17}H_{10}O_2$: C, 82.92; H, 4.07. Found: C, 82.90; H, 4.23. Ultraviolet spectrum (ethanol): λ_{max} 264 (log ϵ 4.69); λ_{max} 287.5 (log ϵ 4.30); λ_{max} 297 (log ϵ 4.42).

B. By carbonation of lithio derivative IV. A solution of *n*-butyllithium in dry ether was prepared from 1-bromobutane (2 ml.), lithium (0.25 g.), and ether (25 ml.). A 5 ml. aliquot of this solution was added to a solution of 5-iodobenzo[a]biphenylene (0.500 g.) in dry ether (10 ml.). After 2 min. the red solution of the lithio derivative IV was saturated with gaseous carbon dioxide and worked up as described above for the product of the Grignard carbonation. The yield of recrystallized acid V was 0.212 g. (56.5%).

When this same preparation was carried out using 5-bromobenzo[a]biphenylene instead of the iodide III the acid V was obtained in 37% yield.

5-Carbomethoxybenzo[a]*biphenylene* (VIII). A mixture of benzo[a]biphenylene 5-carboxylic acid (0.100 g.), thionyl chloride (1.3 ml.) and a trace of pyridine was refluxed for 30 min., then allowed to stand for an additional 15 min. Removal of excess thionyl chloride under vacuum left a dark red residue of the crystalline acid chloride VII. Absolute methanol (6 ml.) was added and the mixture refluxed for 10 min., then evaporated to dryness under reduced pressure. Chromatography of the residue on neutral alumina in benzene afforded the pure ester VIII as orange needles (0.099 g., 94%), m.p. 126–127°, on evaporation of the benzene eluate.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.08; H, 4.61. Found: C, 83.10; H, 4.67.

Benzo[a]*biphenylene-5-carboxamide* (IX). The crude acid chloride VII was prepared from benzo[a]biphenylene-5-carboxylic acid (0.100 g.) as described in the preparation of the methyl ester VIII. A solution of the chloride VII in benzene (5 ml.) was saturated with gaseous dry ammonia. The yellow precipitate was filtered, dried, washed with cold water, and dried once more. Crystallization of the yellow powder from benzene-methanol gave fine yellow needles of amide IX (0.076 g., 76%), m.p. 271–272°. Recrystallization from ethanol afforded the analytical sample, m.p. 273°.

Anal. Calcd. for $C_{17}H_{11}NO$: C, 83.24; H, 4.52; N, 5.71. Found: C, 83.42; H, 4.74; N, 5.83.

5-Cyanobenzo[a]*biphenylene* (X). *A. From Iodide* III. A mixture of cuprous cyanide (0.50 g.), 5-iodobenzo[a]biphenylene (0.50 g.) and dimethylformamide (11 ml.) was refluxed for 3 hr. The cooled solution was diluted with saturated aqueous ferric chloride (5 ml.) followed by sufficient cold water to effect complete precipitation of the product. The orange precipitate was filtered, dried, dissolved in benzene and chromatographed on alumina. The nitrile X moved down the column as a strong orange band, which was eluted with benzene. Concentration of the eluate yielded, in two crops, fine orange needles of 5-cyanobenzo[a]biphenylene (0.29 g., 84%). The first crop (0.21 g.), m.p. 154–155°, was of analytical purity.

Anal. Calcd. for $C_{17}H_9N$: C, 89.84; H, 3.99; N, 6.17. Found: C, 89.60; H, 3.83; N, 6.03. Ultraviolet spectrum (ethanol): λ_{max} 239 (log ϵ 4.43); λ_{max} 270 (log ϵ 4.73); λ_{max} 290 (log ϵ 4.42); λ_{max} 299.5 (log ϵ 4.42).

B. From benzo[a]*biphenylene-5-carboxamide* (IX). A solution of amide IX (0.143 g.) in thionyl chloride (3.0 ml.) was refluxed for 5 min. Excess thionyl chloride was removed under vacuum and the red residue was dissolved in ether. The ethereal solution was washed successively with water, dilute sodium hydroxide, and again with water. The solution was dried over magnesium sulfate, evaporated, and the residue dissolved in benzene and chromatographed on alumina. Elution of the orange band and evaporation of the eluate afforded 5-cyanobenzo[a]biphenylene (0.097 g., 70%), m.p. 153–154°. Recrystallization from benzene gave small orange needles, m.p. 154–155°. The melting point was not depressed by a sample of nitrile prepared by the cuprous cyanide method, and the infrared spectra of both samples were identical.

5-Acetylbenzo[a]*biphenylene* (XI). *A. From 5-cyanobenzo*[a]*biphenylene* (X). A solution of the nitrile X (0.200 g.) in benzene (2 ml.) was added to 4*M* ethereal methylmagnesium bromide (4 ml.) and the mixture was refluxed for 5 hr. The cooled red solution was diluted with ether and shaken with cold aqueous ammonium chloride. The organic layer was then extracted with cold dilute sulfuric acid and the aqueous acidic extract, which contained the intermediary ketimine as the sulfate, was allowed to stand overnight at room temperature to effect hydrolysis of the imine to the ketone. Extraction of the cloudy yellow solution with ether and evaporation of the dried ether phase gave a red oil which resisted crystallization. 2,4,7-Trinitrofluorenone (0.040 g.) was added to a solution of this oil in a small volume of benzene and the mixture was heated to effect complete solution. Addition of excess methanol to the hot benzene solution caused the separation of the crude 2,4,7-trinitrofluorenone derivative of XI as a deep purple precipitate, which was filtered, dried, and dissolved in benzene. Chromatography on alumina and elution of the principal orange-red band afforded, after concentration of the benzene eluate and addition of 30–60° petroleum ether, red needles (0.024 g., 11%) of 5-acetylbenzo[a]biphenylene, m.p. 85–86°.

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.34; H, 4.89. Ultraviolet spectrum (ethanol): λ_{max} 246 (log ϵ 4.18); λ_{max} 267 (log ϵ 4.61); λ_{max} 297 (log ϵ 4.35).

B. From Benzo[a]*biphenylene-5-carboxylic acid* (V). The acid V (0.100 g.) was converted into the acid chloride VII as described in the preparation of the methyl ester VIII. The crude chloride VII, dissolved in dry benzene (25 ml.) was added at room temperature to an ethereal solution (10 ml.) of dimethylcadmium containing an excess (*ca.* 1 g.) of cadmium reagent. After 5 min. the red turbid solution was diluted with ether and shaken with cold 10% hydrochloric acid. The organic layer was washed with water and dilute sodium carbonate, dried, and evaporated to dryness to yield the almost pure red crystalline ketone XI (0.092 g., 93%), m.p. 80–84°. Chromatography of this material in benzene on alumina afforded completely pure ketone, m.p. 85.5–86.5°. This material was identical with that prepared from nitrile X, as evidenced from mixed melting point and infrared comparisons.

Attempted acetylation of benzo[a]*biphenylene* (I). Benzo[a]biphenylene (0.400 g.) was dissolved in carbon disulfide (40 ml.) and aluminum chloride (0.300 g.) and acetyl chloride (2.1 ml.) were added. The purple mixture was refluxed for 45 min. and then treated with dilute hydrochloric acid to decompose the aluminum chloride complex formed Extraction with ether afforded, after usual workup conditions, a red oil which was dissolved in benzene and chromatographed on Woelm neutral alumina (activity grade II) to yield unchanged hydrocarbon I (0.150 g.) and two orange bands containing red oils (0.147 g. and 0.089 g., respectively). Neither red oil could be seeded by authentic 5-acetylbenzo[a]biphenylene (XI) and both oils had ultraviolet and infrared spectra quite different from those of authentic ketone XI.

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