TABLE I

ESTERS

Ester	Yield, %	M.p., °C	Solvent	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-$MesCO_2C_6H_4CODur$	86	181.0–183.0	Ethyl acetate	80.97	80.83	7.05	7.28
p-$CH_3CO_2C_6H_4CODur$	84	103.5–104.5	Ethanol	77.00	76.95	6.83	7.02
p-$C_6H_5CO_2C_6H_4CODur$	60	188.0–189.0	Ethyl acetate	80.42	80.29	6.18	6.33
p-$C_6H_5SO_2OC_6H_4CODur$	58	133.5–134.5	Ethanol	70.02	69.75	5.62	5.76

The phenol was also prepared by hydrolysis of duryl *p*-methoxyphenyl ketone. To 3.0 g. of this compound was added 6 ml. of 48% hydrobromic acid and 8 ml. of glacial acetic acid. The solution was boiled overnight and poured into water. The product was recrystallized from benzene; yield 1.8 g. (62%).

Synthesis of Esters.—All the esters were prepared by standard methods and are listed in Table I together with melting points, yield, solvents and analytical data.

Reaction of the Esters with *t*-Butylmagnesium Chloride.—The procedure was substantially the same in every case and is illustrated by that employed with the acetate which is described below.

***p*-Acetoxyphenyl Duryl Ketone and *t*-Butylmagnesium Chloride.**—A Grignard reagent was prepared from 4.8 g. of magnesium, 20.2 g. of *t*-butyl chloride and 150 ml. of ether. To this solution was added 11.8 g. of *p*-acetoxyphenyl duryl ketone in 150 ml. of dry benzene. The solution turned reddish-brown and was stirred under reflux overnight. The mixture was poured into a mixture of ice and dilute hydrochloric acid. The ether layer was washed with water and dried with sodium sulfate. Evaporation of the solvent left an oil which crystallized when cooled. The ketone was recrystallized from ethanol (Darco); yield 7.8 g. (70%); m.p. 126.0–127.0°. A mixture melting point with an authentic sample of *p*-*t*-butylphenyl duryl ketone showed no depression.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE OAK RIDGE NATIONAL LABORATORY]

Studies in the Wagner Rearrangement.[1,2,3] II. The Synthesis and Structure Determination of Benz[a]anthracene-5,6-C_1^{14}

BY CLAIR J. COLLINS, JOHN G. BURR, JR., AND DANIEL N. HESS

The synthesis of benz[a]anthracene-5,6-C_1^{14} is reported in an over-all yield, from carbon-C^{14} dioxide, of 76%. Degradation of this labeled hydrocarbon indicates that the radioactivity is distributed between positions 5 and 6 of the benz[a]anthracene structure in the ratio 48:52.

Introduction

The synthesis of phenanthrene-9-C^{14} through the Wagner rearrangement of 9-fluorene(methanol-C^{14}) has been reported.[1] In order to demonstrate the generality of the procedure as a synthetic process for introducing isotopic carbon into aromatic polynuclear hydrocarbons, and to study the directive influence of various substituents on the course of this reaction, the method has been applied to the preparation of unsymmetrically substituted derivatives of phenanthrene. The synthesis and structure determination of benz[a]anthracene-5,6-C_1^{14} (VI), the first of these, is now reported.

11H-Benzo[b]fluorene-11-one[4] (I) was converted to the hydrocarbon (II) by hydrogenation in the presence of a large excess of 10% palladium-on-carbon catalyst. The hydrocarbon was then converted to benz[a]anthracene-5,6-C_1^{14} (VI) through compounds III, IV and V by a series of reactions analogous to those described[1] for the synthesis of phenanthrene-9-C^{14}.

Since the structures for both the carbinol (V) and the hydrocarbon (VI) are unsymmetrical, the carbonium ion intermediate which may be written in the dehydration of 11H-benzo[b]fluorene-11-(methanol-C^{14}) (V) might conceivably rearrange in either one or both of two ways to produce benz[a]anthracenes labeled in the 5-position, the 6-position, or in both of these positions. The degradative scheme shown in the reaction series VI → XI was employed to locate the radioactivity in structure VI.

The labeled benz[a]anthracene (VI) was oxidized to the dihydrodiol (VII) with osmium tetroxide.[5] Attempts to cleave VII with lead tetraacetate failed. Treatment with chromium trioxide in acetic acid yielded 5,6-benz[a]anthraquinone (VIII), however, which was converted to the dibasic acid (IX) with hydrogen peroxide. Although this acid, upon distillation at atmospheric pressure, was converted to a mixture of the keto-acid (X) and the ketone (XI), the acid (X) could be obtained in much higher yield from the dicarboxylic acid (IX) by cyclization with sulfuric acid.[6] Fieser and Dietz assigned X as the probable structure of this keto-acid. We have confirmed this structure by decarboxylation of X in quinoline with basic copper carbonate catalyst, to the known ketone XI, whose identity was demonstrated by comparison with an authentic sample.[7] The

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[1] Paper I in this series: C. J. Collins, THIS JOURNAL, **70**, 2418 (1948).

[2] This paper is based upon work performed under Contract Number W-7405, eng. 26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

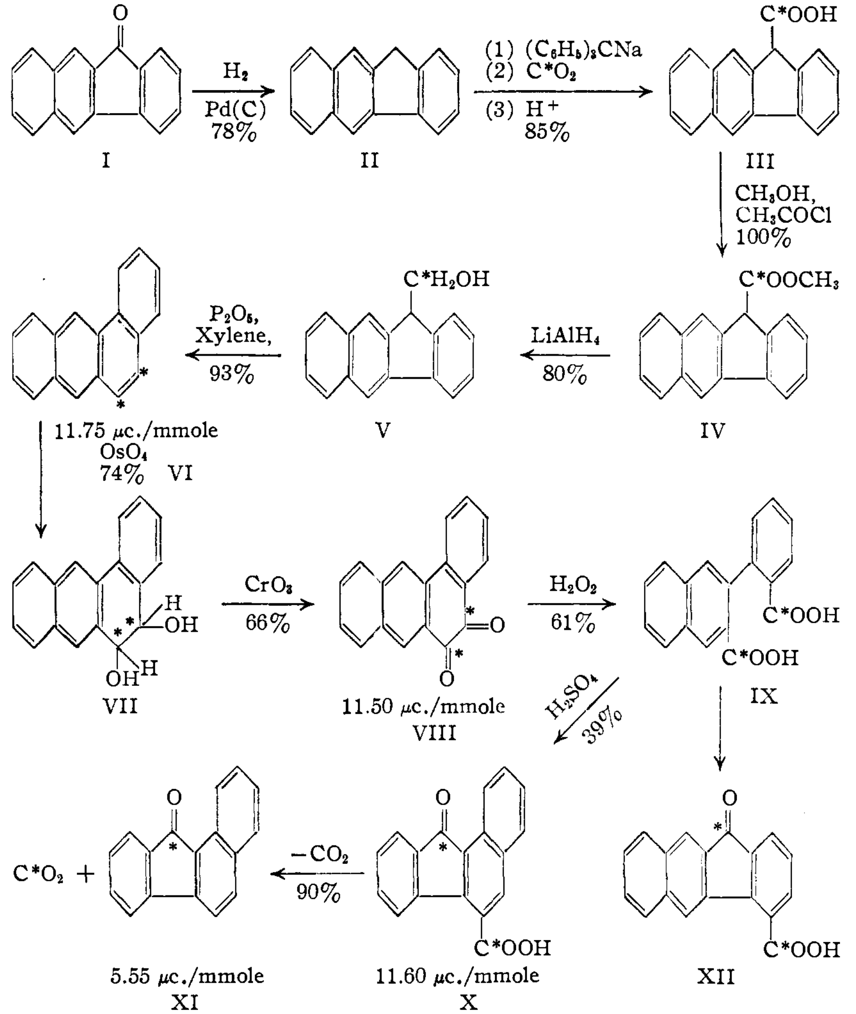
[3] Presented before the Division of Organic Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Illinois, September, 1950.

[4] J. Thiele and A. Wanscheidt, *Ann.*, **376**, 269 (1921).

[5] J. W. Cook and R. Schoental, *J. Chem. Soc.*, 172 (1948).

[6] L. F. Fieser and E. M. Dietz, THIS JOURNAL, **51**, 3143 (1929).

[7] M. Orchin and L. Reggel, *ibid.*, **73**, 439 (1951). These authors kindly furnished us with their experimental procedure for the synthesis of compound XI (not labeled) prior to publication of their paper. The Orchin-Reggel synthesis was performed in this Laboratory by Dr. A. Russell Jones.



other possible structure (XII) for the keto-acid obtained by ring closure of IX would be expected upon decarboxylation, to yield 11H-benzo[b]-fluorene-11-C^{14}-one. This ketone (I, labeled) was not isolated.

Decarboxylation of the keto-acid X removes from this compound the carbon atom which had its origin in the 6-position of the radioactive benz[a]-anthracene (VI). The radioactivity, therefore, of the ketone (XI) which results from this decarboxylation represents the carbon-14 present in the 5-position of hydrocarbon VI. The results of carbon-14 assays for compounds VI, VIII, X and XI are shown by the appropriate structures, and are expressed as microcuries per millimole (μc./mmole) of compound. From these data it is apparent that the activities of positions 5 and 6 of benz[a]anthracene-5,6-C$_1^{14}$ (VI) are, respectively, 5.55 and 6.05 microcuries of carbon-14 per millimole, and that these values are in the ratio of 48:52. This represents a difference in molar radioactivities for these two positions greater than the experimental error inherent in the carbon-14 determinations. The ratio, however, is too near unity to be assigned a significance in the rearrangement tendencies of the carbonium ion intermediate which may be written in the dehydration of the carbinol V.

Experimental[8]

11H-Benzo[b]fluorene (II).—A suspension of 2.55 g. of the ketone (I)[4] in 75 ml. of ethanol was mixed with 6 g. of Hartung palladium-on-carbon catalyst[9] and hydrogenated at atmospheric pressure for 19 hours. The solution was filtered, and the catalyst was extracted several times with benzene. Combination and evaporation of the extracts gave a residue which after crystallization from ethanol–benzene yielded 1.85 g. (78%) of 11H-benzo[b]fluorene (II) as white needles melting at 210–211°.

11H-Benzo[b]fluorene-11-(carboxylic-C^{14}) Acid (III).—To 250 mg. of 11H-benzo[b]fluorene (II) was added, in an atmosphere of helium, 7 ml. of an ethereal solution of triphenylmethylsodium containing 0.16 mmole of sodium per ml. The mixture quickly became deep purple. The flask containing this derivative was surrounded with a liquid nitrogen trap and evacuated to a few microns pressure. The carbon dioxide generated from 251 mg. of barium carbonate (1.27 mmoles; specific activity, 29.8 microcurie/mmole) was distilled into the flask containing the sodio derivative. The flask was isolated from the vacuum system and warmed. The color disappeared as the mixture became fluid, and a pale tan precipitate formed. The mixture was hydrolyzed with 20 ml. of water and submitted to a continuous ether extraction. The ether fraction yielded 356 mg. of a hydrocarbon mixture consisting chiefly of triphenylmethane. The alkaline aqueous solution in the extractor was acidified with concentrated hydrochloric acid and resubmitted to ether extraction. Evaporation of the ether gave 255 mg. (85%) of a white solid which after crystallization from benzene weighed 200 mg. and melted at 247–248°.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.1; H, 4.61. Found: C, 83.1; H, 5.16; 29.7 microcuries of carbon-14 per millimole.

Methyl 11H-Benzo[b]fluorene-11-(carboxylate-C^{14}) (IV).—To a solution of 86.8 mg. of the acid (III) in 10 ml. of methanol was added 5 drops of acetyl chloride. After one hour the solution was evaporated to dryness. The residue, 90.8 mg. of the methyl ester (IV), (100%) melted at 117–118°.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.10. Found: C, 83.3; H, 5.70; 29.7 microcuries of carbon-14 per millimole.

11H-Benzo[b]fluorene-11-(methanol-C^{14}) (V).—The supernatant liquid from the solution of 0.4 g. of lithium aluminum hydride in 20 ml. of ether was added to a solution of 78 mg. of the methyl ester (IV) in 15 ml. of ether. This solution was stirred for 20 minutes and was hydrolyzed with moist ether, followed by 6 *N* hydrochloric acid. The ethereal layer was washed with aqueous sodium carbonate, then water, then dried and concentrated. The residue was dissolved in benzene and passed through a small column of alumina. Repeated elution with benzene removed 23.7 mg. of a yellow resin, which was discarded. Elution with ab-

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(8) Melting points were taken on a Fisher–Johns block, and are uncorrected. Carbon-14 assays were carried out as reported previously,[1] using ion current measurements. Microanalyses for carbon and hydrogen were performed by P. Z. Westerdahl, Chemistry Division, Oak Ridge National Laboratory.

(9) E. R. Alexander and A. C. Cope, THIS JOURNAL, **66**, 888, footnote 7 (1944).

solute ethanol then removed 56.0 mg. (80% yield) of carbinol, which solidified after trituration with benzene to white crystals melting at 166–168°.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.8; H, 6.50. Found: C, 87.6; H, 6.4; 29.2 microcuries of carbon-14 per millimole.

Benz[a]anthracene-5,6-C_1^{14} (VI).—Ten ml. of xylene was distilled from phosphorus pentoxide into a flask containing 30 mg. of the carbinol (V). About 0.5 g. of phosphorus pentoxide was added to the flask, and the mixture was heated under reflux for 35 minutes. The mixture was then hydrolyzed with 25 ml. of water, and submitted to continuous ether extraction for 15 hours. Evaporation of the ether–xylene extract gave 28.1 mg. of a solid which, when dissolved in benzene and passed through a small alumina column, yielded 26.5 mg. (93%) of an orange solid, melting at 138–144°. One crystallization from ethanol gave a white product which melted at 156–157°. This melting point was not depressed by admixture with a sample of authentic benz[a]anthracene. The picrate, melting at 137–138°, melted at the same temperature when mixed with authentic benz[a]anthracene picrate.

Anal. 29.4 microcuries of carbon-14 per millimole of compound VI.

High Level Preparation of Benz[a]anthracene-5,6-C_1^{14} (VI).—The acid (III) was prepared from 3.68 millimoles of 11H-benzo[b]fluorene, 2.88 millimoles of triphenylmethylsodium and an excess (3.57 millimoles) of carbon-C^{14} dioxide, the yield being 2.45 millimoles. This was converted to 2.19 millimoles of benz[a]anthracene-5,6-C_1^{14} (VI) by the same procedure used for the high level synthesis[1] of phenanthrene-9-C^{14}. The over-all yield of VI, based on either the triphenylmethylsodium or unrecovered carbon-C^{14} dioxide, was 76% (2.19 millimoles). Purification of VI was effected by crystallization from ethanol, rather than by formation of the picrate. A 10.2-mg. sample was diluted with 2100 mg. of inactive benz[a]anthracene, and the mixture, after homogenization, was twice crystallized from benzene and assayed.

Anal. 11.75 microcuries of carbon-14 per millimole of diluted compound VI.

The undiluted benz[a]anthracene-5,6-C_1^{14} possessed therefore a millimolar activity of 2.43 millicuries of carbon-14. The diluted sample (millimolar activity 11.75 microcuries) was used for the degradative sequence VI–XI.

5,6-Dihydrobenz[a]anthracene-5,6-diol-5,6-C_1^{14} (VII).—A sample of VI (930 mg., 11.75 microcuries of carbon-14 per millimole) was dissolved in 40 ml. of benzene in a 250-ml. glass stoppered bottle. A 1-g. vial of osmium tetroxide was broken in the bottle, and 1 ml. of pyridine was added. The bottle was stoppered, the contents were stirred with a magnetic bar for one hour, and allowed to stand for two days. At the end of this time, 50 ml. of methylene dichloride and 100 ml. of 3% potassium hydroxide containing 10 g. of mannitol were added, and the bottle was mechanically shaken for five hours. The heavy organic layer was then separated, and evaporated to dryness in an air stream at room temperature. The residue was taken up in a benzene–chloroform mixture, filtered, and the filtrate was evaporated to dryness. The residue was crystallized from chloroform to give 773 mg. (74%) of the diol (VII) as a white solid, melting at 205–206° [lit.[6] 202–204°].

5,6-Benz[a]anthraquinone-5,6-C_1^{14} (VIII).—The diol (VII, 773 mg.) was dissolved in 25 ml. of acetic acid, and this solution was mixed with a solution of 0.78 g. of chromium trioxide in a mixture of 1.5 ml. of water and 13.5 ml. of acetic acid. A heavy red precipitate formed immediately and, after standing for 15 minutes, the mixture was chilled and filtered. The product was 432 mg. of orange-red quinone (VIII) melting at 263–265° [lit.[6] 262–263°]. The filtrate was added to the residual material from the diol preparation, another 0.5 g. of chromium trioxide was added, and the solution was allowed to stand an additional 15 minutes prior to evaporation in an air stream. The residue was stirred with water, and the precipitate was filtered and washed with alcohol, yielding an additional 255 mg. (89%) of the 5,6-benz[a]anthraquinone-5,6-C_1^{14} (VIII).

Anal. 11.50 microcuries of carbon-14 per millimole.

2-Phenylnaphthalene-2′,3-(dicarboxylic-C_1^{14}) Acid (IX).—A solution of the quinone (VIII, 688 mg.) in 70 ml. of acetic acid was heated on the steam-bath, and to it was added 0.45 ml. of 30% hydrogen peroxide. After an hour, a second and similar addition of peroxide was made, and heating was continued another hour. After standing overnight, a third addition of peroxide was made and the solution was evaporated on the steam-bath in an air stream. The residue was washed with water by decantation, and then warmed with aqueous sodium bicarbonate solution. An orange powder (221 mg.) was insoluble in the bicarbonate solution. The cold solution was slowly acidified with concentrated hydrochloric acid. The precipitated acid, after filtering and air drying, weighed 445 mg. (61%) and melted at about 130°. A sample was dissolved in hot dilute methanol. The solution was cooled, decanted from a tar which precipitated, and then chilled. The light purple micro needles which deposited melted at 243–246° (lit.[6] 246°).

11H-Benzo[a]fluorene-11-C^{14}-one-6-carboxylic Acid and 11H-Benzo[a]fluorene-11-one-6-(carboxylic-C^{14}) Acid (X).[10]—A 430-mg. sample of the crude dibasic acid (IX) was dissolved in about 40 ml. of 98% sulfuric acid. The dark green solution was allowed to stand for two hours, and was then poured onto ice. The resulting suspension was filtered, and the brown precipitate was dissolved in boiling toluene. An insoluble residue of about 0.1 g. remained. The toluene filtrate was concentrated to 20 ml., and at this point 39% of the keto-acid (X) precipitated as an orange amorphous powder melting at 250–255°. Recrystallization of 240 mg. of the acid (obtained from another run) from toluene, gave after boiling with Norite, 168 mg. of pure acid as yellow needles, melting at 267–268° (lit.[6] 268°).

Anal. 11.60 microcuries of carbon-14 per millimole.[11]

11H-Benzo[a]fluorene-11-C^{14}-one (XI).—A 160-mg. sample of X (6.83 microcurie of carbon-14) was dissolved in 15 ml. of quinoline, and 200 mg. of basic copper carbonate was added. The mixture was refluxed for 15 minutes (with carbon dioxide sweep) in an apparatus designed to collect in an ion chamber any evolved gases. Measurement of the activity in the ion chamber showed 3.43 microcurie of carbon 14 present (50% of the total activity of X[12]). The quinoline solution was filtered from the brown copper oxide, and was poured into dilute hydrochloric acid. The precipitated orange solid was extracted with ether and benzene. The ether–benzene solution was dried and evaporated. The resulting orange solid was passed, in benzene solution, through an alumina column; and the solvent was evaporated from the eluate. The residue was 112 mg. (90%) of an orange crystalline solid (XI). This was crystallized from pentane to give 76 mg. of orange needles melting at 132–133°. These crystals showed no melting point depression when mixed with an authentic sample.[7]

Anal. 5.49, 5.61 microcuries of carbon-14 per millimole.

The ketone (XI) was also obtained directly from IX, when 400 mg. of IX was heated with a free flame at atmospheric pressure, and finally distilled at a pressure of 22 mm. The orange-yellow sublimate weighed 310 mg. From this sublimate were isolated 47 mg. of the keto-acid (X) melting at 261–262°, and 34 mg. of the ketone (XI) melting at 125–130°.

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(10) The contents of the mixture (X) differ only in their positions of labeling. Each of the labeled species is considered to possess one carbon-14 atom in any given molecule. To name this mixture "11H-benzo[a]fluorene-11-C^{14}-one-6-(carboxylic-C^{14}) acid" would imply the presence of two carbon-14 atoms in each labeled molecule. Owing to the authors' inability to find a single proper name for compound X, each labeled component has been named separately.

(11) This value is an average of eight separate determinations.

(12) Since this decarboxylation reaction can hardly be considered quantitative, the collected carbon-C^{14} dioxide was assayed only to provide a rough check for the extent of decarboxylation. In calculating the ratio of carbon-14 distribution between positions 5 and 6 of the benzanthracene structure the more precise value of the millimolar activity of compound XI was used.