removal of solvent and fractional distillation yielded 0.6 g. of the methyl ester of C, b.p. 110–116°, which was refluxed for 36 hr. in a solution of 0.06 g. of sodium in 20 cc. of methanol. The cooled mixture was neutralized with gaseous hydrogen chloride, filtered from sodium chloride and freed of solvent by distillation. Evaporative distillation of the residue afforded 0.2 g. of *rac*-methyl α-methylbutyrate from which water containing 0.04 ± 0.01 wt. % of deuterium oxide was obtained.

When 10.0 g. of optically pure carbinol, $[\alpha]^{27}\mathrm{D}$ −5.81° (neat), is oxidized by the procedure applied to B, 6.0 g. of α-methylbutyric acid, $[\alpha]^{27}\mathrm{D}$ +17.75° (neat), 98% optically pure, was obtained. Reaction of 3.6 g. of this acid with excess diazomethane and fractional distillation of the product gave 1.22 g. of methyl α-methylbutyrate, b.p. 112–115°, $[\alpha]^{27}\mathrm{D}$ +21.1° (*c* 1.7, methanol). A solution of 1.2 g. of this ester in 25 cc. of methanol containing 0.1 g. of sodium was not racemized on standing 24 hr. at room temperature, but was completely racemized on refluxing for 30 hr.

(b) **Aluminum Alkoxide-catalyzed.**—By a procedure similar to the previous one, 15.0 g. of $(-)_{99\%}$-2-methylbutanol-1-$d_{47.3\%}$ was heated at 120° for 40 hr., with 5 mole % each of aluminum isopropoxide and benzophenone. Carbinol was isolated, refluxed with 400 cc. of water for 24 hr. and purified by distillation to give 10.0 g. of $(-)_{48\%}$-2-methyl-2-$d_{8.9\%}$-butanol-1. Five grams of this material was oxidized with alkaline permanganate to 2.7 g. of α-methyl-α-$d_{8.9\%}$-butyric acid, b.p. 173–174°, $[\alpha]^{27}\mathrm{D}$ +10.4° (methanol), from which water of combustion containing 0.98 ± 0.02 wt. % of deuterium oxide was obtained.

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

Studies in the Wagner Rearrangement.[1-3] III. Chrysene-5,6-C$_1^{14}$

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Chrysene-5,6-C$_1^{14}$ was produced in quantitative yield through the dehydration–rearrangement of 11H-benzo[a]fluorene-11-methanol-C^{14}. The distribution of radioactivity between the 5- and 6-positions of the chrysene so prepared has been shown to be in the ratio 76:24. These results are discussed in terms of the presumed carbonium ion intermediates. The over-all yield of chrysene-5,6-C$_1^{14}$, in the four-step synthesis from carbon-C^{14} dioxide, was 93%.

Introduction

The synthetic method used for incorporating carbon-14 into phenanthrene[1a] and benz[a]anthracene[1b] has now been extended to the preparation of labeled chrysene V. Although the radioactivity was nearly equally divided between the two labeled positions of benz[a]anthracene-5,6-C$_1^{14}$ (48% in the 5-position and 52% in the 6-position), the chrysene V contains more than three times as much carbon-14 in the 5- as in the 6-position.

The compounds involved in the synthesis of chrysene-5,6-C$_1^{14}$ are shown in the reaction sequence I → V; the degradative scheme used to establish the partition of radioactivity between the two labeled positions is indicated by structures V → XIII. The former sequence parallels those employed for phenanthrene[1a] and benz[a]anthracene,[1b] and requires no further discussion. The latter scheme is noteworthy however, both because it provides two separate checks on the carbon-14 distribution in hydrocarbon V, and because it clears up the confusion which previously existed[6,7] concerning the structures of keto acids VIII and XI.

Labeled chrysene V was oxidized to chrysenequinone VI with chromic acid.[6] The quinone VI was then converted to the dicarboxylic acid VII either through the Beckmann rearrangement of the quinone monoöxime and hydrolysis of the resulting amides,[7] or by its direct oxidation with hydrogen peroxide. Graebe and co-workers[6,7] reported that a keto acid melting at 283° and corresponding to structure VIII was obtained either when the monoöxime of the quinone was subjected to a Beckmann rearrangement at 130–140°, or when the dicarboxylic acid VII was treated with sulfuric acid for periods of 12 to 24 hours at room temperature. Structure VIII was assigned this compound on the basis of its failure according to "von Meyer's rule," to form a methyl ester when heated for 24 hours with methanol saturated with hydrogen chloride. Graebe and Gnehm[8] reported also that this keto acid on being heated with soda lime yielded 11H-benzo[a]fluorene-11-one (XIII) while, when distilled with zinc dust, it was converted to 11H-benzo[a]fluorene (I). These authors said, "It was not possible for us to solve this paradox."[8]

We have now shown that the action of sulfuric acid on compound VII causes the formation of two keto acids, VIII and XI. Further, the keto acid which melts at 283° possesses structure XI rather than structure VIII. Contrary to the observations of Graebe and Gnehm, keto acid XI is easily esterified when heated in methanol containing a trace of acetyl chloride, while keto acid VIII remains unesterified; this difference in ease of esterification was used in fact to separate these two compounds. There can be no doubt of these structures since, on decarboxylation, the two compounds yielded the known ketones X and XIII, respectively. Structures VIII and XI are also confirmed by the radiochemical data.

Radioactivities are shown by the appropriate

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(1) Previous papers: (a) I, C. J. Collins, THIS JOURNAL, **70**, 2418 (1948); (b) II, C. J. Collins, J. G. Burr and D. N. Hess, *ibid.*, **73**, 5176 (1951).

(2) This paper is based upon work performed under contract Number W-7405-eng-26 for the Atomic Energy Commission at Oak Ridge National Laboratory.

(3) Presented in part before the Division of Organic Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950.

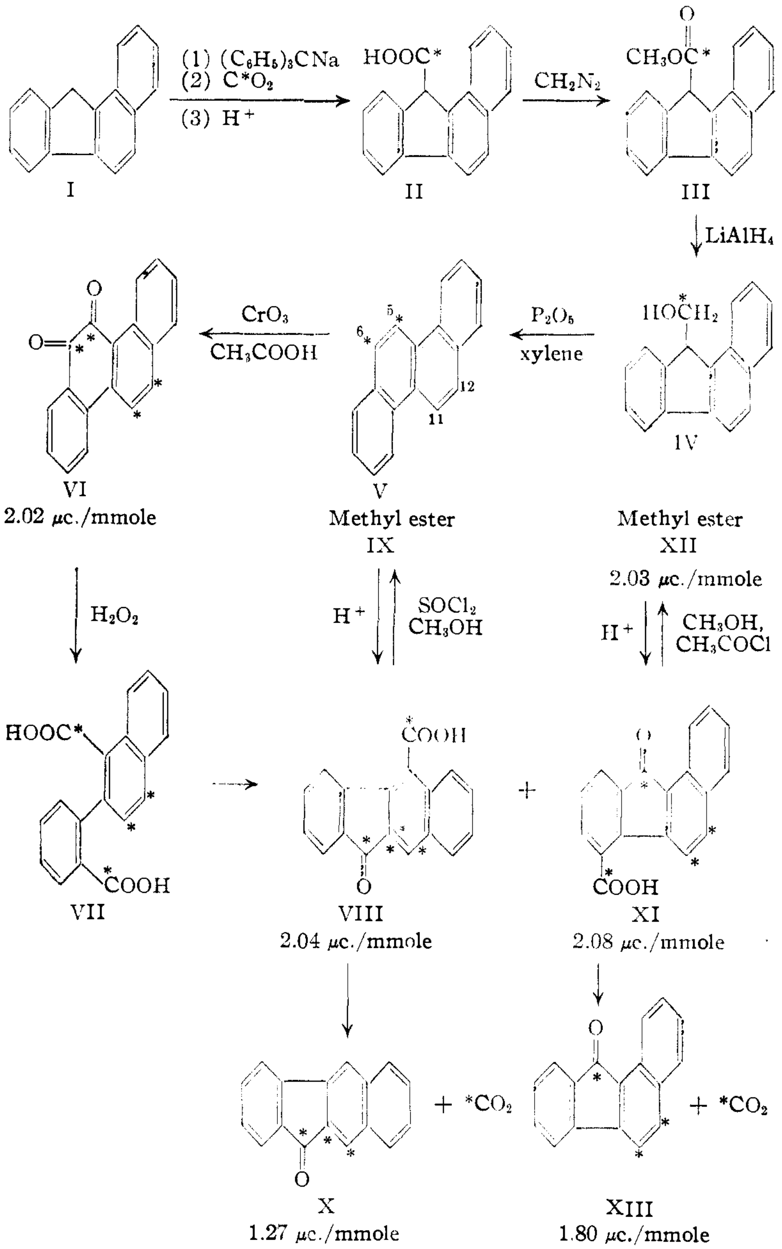
(4) Visiting Consultant to Oak Ridge National Laboratory, June–September, 1950.

(5) Member of the Research Participation Program jointly sponsored by the Oak Ridge Institute of Nuclear Studies and the Oak Ridge National Laboratory, March–June, 1950.

(6) C. Graebe and F. Honigsberger, *Ann.*, **311**, 257 (1900).

(7) C. Graebe and R. Gnehm, Jr., *ibid.*, **335**, 113 (1904).

(8) Reference 7, p. 120.



structural formulas, and are expressed as microcuries per millimole (μc./mmole). The labeled positions in each structure are designated by asterisks. The calculation from these data of the positional radioactivities of hydrocarbon V must allow for the fact that positions 5 and 6 are identical with positions 11 and 12 of the chrysene structure. The quinone VI is therefore shown as labeled in four positions. The following relations are apparent

$x + y = 2.04$ μc (average millimolar radioactivities of VI, VIII, XI and XII, assumed to be the millimolar radioactivity for V) (1)

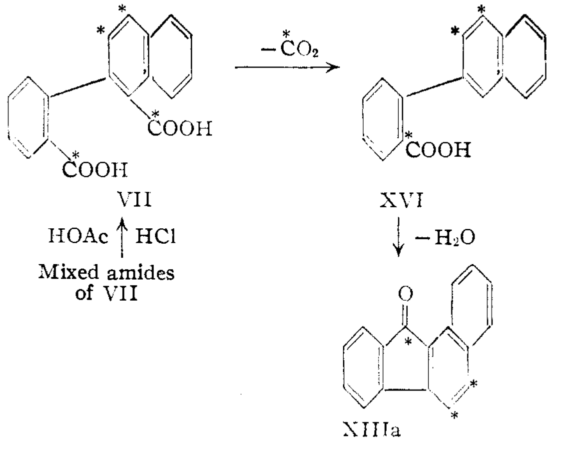
$\frac{x}{2} + y = 1.27$ μc.(millimolar radioactivity of X) (2)

$x + \frac{y}{2} = 1.80$ μc.(millimolar radioactivity of XIII) (3)

where x and y are the millimolar radioactivities of chrysene-5-C^{14} and chrysene-6-C^{14}, respectively, in the mixture V. From equations (1) and (2), x = 1.54 μc., y = 0.50 μc. From equations (1) and (3), x = 1.56 μc., y = 0.48 μc. These two independent data, in close agreement, indicate that the carbon-14 in the hydrocarbon V is divided between positions 5 and 6 in the ratio 76:24.

During the preparation of the dicarboxylic acid VII by our modification of the method of Graebe and Gnehm,[7] an interesting observation was made concerning the acid-catalyzed decarboxylation and ring-closure of VII to XIII at 150°. In the latter procedure, the oxime of labeled chrysenequinone VI was subjected to a Beckmann rearrangement to yield the mixed amides of VII. When these mixed amides were heated at 150° in a mixture of acetic and hydrochloric acids (4:1), 70% of the material was converted to the dicarboxylic acid VII. A 30% yield of 11H-benzo[a]fluorene-11-one-5,6,11-C_1^{14} (XIIIa) was also obtained. The ketone prepared by this method, although structurally identical with XIII, obtained by the decarboxylation of XI, contains a different carbon-14 distribution, and will be referred to as XIIIa. The molar radioactivity of XIIIa was 64.5% that of the dicarboxylic acid VII from which it had been formed. These results can only mean that the major portion of ketone XIIIa had been formed by a completely different mechanism than VII → XI → XIII. (The ketone XIII formed through the path VII → XI → XIII contained 88.3% of the carbon-14 originally present in the dicarboxylic acid VII.)

From these data it can be calculated that 92% of the carbon present in the 11-position of XIIIa *had its origin in the 6-position of chrysene-5,6-C_1^{14} (V)*. This observation supports the mechanism VII →



XVI → XIIIa for the formation of the major portion (92%) of this ketone during the hydrolysis of the mixed amides of VII. The remaining 8% could have been formed through the alternate (VII → XI → XIII) path.

Experimental Part

11H-Benzo[a]fluorene (I).—11H-Benzo[a]fluorene-11-one[9] was converted to the hydrocarbon I by catalytic[10] reduction[1b]; yield 1.76 g. (from 3.00 g. of I), m.p. 184.4–184.8° (lit.[11] 185.4–186.0).

11H-Benzo[a]fluorene-11-carboxylic-C^{14} Acid (II).—In a typical preparation the carbon-C^{14} dioxide generated from 633 mg. of barium carbonate-C^{14} was used to carbonate the sodium derivative prepared from 651 mg. of hydrocarbon I and 14 ml. of an ethereal solution of triphenylmethylsodium.[1a,1b] The procedure was the same as that previously described.[1a,1b] The yield of acid II was 660 mg. (83%) white needles whose m.p. after one crystallization from benzene was 218–221° with decomposition. In later runs it was found that the yield could be increased to nearly 100% by: (a) distillation of the carbon dioxide–ether mixture from the flask after carbonation had been completed, and recovery of the remaining carbon-C^{14} dioxide; and by (b) shortening the time of continuous ether extraction of the alkaline solution of acid II. The sodium salt of this acid is somewhat soluble in ether, and on prolonged extraction can be almost completely removed from aqueous solution.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.08; H, 4.62. Found: C, 83.11; H, 4.59; microcuries of carbon-14 per millimole of II,[12] 589, 589.

Methyl 11H-Benzo[a]fluorene-11-carboxylate-C^{14} (III).—An excess of an ethereal solution of diazomethane was added to a cooled solution of 146 mg. of acid II in 5 ml. of dry methanol. After 20 minutes the solution was evaporated to dryness, and an ether solution of the product was washed with water. The ether layer yielded 153 mg. of solid material. The solid material was crystallized from methanol. The first crop of crystals (m.p. 133–135°) weighed 50 mg. Two additional crops increased the total yield to 73%. An analytical sample was prepared; m.p. 135.0–135.5°. Several preparations gave similar results.

Anal. Microcuries of carbon-14 per millimole of III, 590, 592, 593, 595.

11H-Benzo[a]fluorene-11-methanol-C^{14} (IV).—In a typical preparation, 0.5 g. of lithium aluminum hydride in ether was added to 5 ml. of an ether solution of 174 mg. of the methyl ester III. After one hour the excess hydride was decomposed with moist ether. The ether solution, after washing with hydrochloric acid, yielded 180 mg. of a yellow oil. All attempts to crystallize this oil failed. When a distillation was attempted, the material decomposed. In order that a solid derivative should be obtained for analysis, the *p*-nitrobenzoate of IV was prepared; white crystals, m.p. 167–167.5°.

Anal. Microcuries of carbon-14 per millimole of *p*-nitrobenzoate of IV, 592.

Chrysene-5,6-C$_1^{14}$ (V).—A sample of carbinol IV (90 mg. of an oil) was dissolved in 20 ml. of dry xylene containing a suspension of about 300 mg. of phosphorus pentoxide. The mixture was heated under a reflux condenser for 30 minutes; the solvent was then removed by directing a dry air-stream over the warm mixture. An excess of aqueous sodium bicarbonate solution was added to the residue. Continuous ether extraction afforded 79 mg. of crude chrysene which was purified by crystallization from a benzene solution which had been passed through a column of alumina. In this way two crops (20 and 23 mg., 65%) of chrysene-5,6-C$_1^{14}$ were obtained; m.p. 252–254°, undepressed when mixed with an authentic sample (lit.[13] 254.5–255°). The product from a previous run was assayed for carbon-14 by the double dilution method.[14]

Anal. Microcuries of carbon-14 per millimole of V, 585.

High Level Preparation of Chrysene-5,6-C$_1^{14}$ (V).—In this preparation the sequence I → V was carried out without purification of materials at any intermediate stage. The acid II was prepared from 3.57 mmoles (10.5 mc.) of carbon-C^{14} dioxide (measured manometrically), 3.45 mmoles of triphenylmethylsodium in ether solution (titrated value) and 4.00 mmoles (871 mg.) of I. By distilling the carbonation mixture to dryness, 0.11 mmole (3.1%) of the carbon-C^{14} dioxide was recovered unreacted. Treatment of the unpurified acid II in methanol with diazomethane in ether produced 3.20 mmoles (876 mg.) of the ester III. The action of lithium aluminum hydride on III produced 876 mg. of an oil IV which yielded 733 mg. (3.21 mmoles) of crude chrysene-5,6-C$_1^{14}$ (V) when heated with phosphorus pentoxide in xylene. The chrysene, when crystallized from acetic acid, yielded a first crop of white crystals (286.9 mg., m.p. 252–254°). Two subsequent crops (111 mg., m.p. 247–253°), and a residue (335 mg. of brown, crystalline material which was not further purified) were also obtained. The over-all yield of crude chrysene-5,6-C$_1^{14}$(V) was 93%.

Anal. Millicuries of carbon-14 per millimole of undiluted V, 2.94.

5,6-Chrysenequinone-5,6,11,12-C$_1^{14}$ (VI).—A portion of the material from the high-level preparation of V was diluted with about 800–1000 times its weight of crude chrysene (Reilly Tar and Chemical Company Technical Grade). The crude diluted product was not assayed for carbon-14, but 14.44 g. of this material was converted directly to the quinone by the method of Graebe and Honigsberger[6] using 62 g. of sodium dichromate and 140 ml. of glacial acetic acid; yield 11.54 g. of quinone, m.p. 228–240°. After one crystallization from acetic acid, the yield was 8.92 g., m.p. 238–240° (lit.[6] 239.5°).

Anal. Microcuries of carbon-14 per millimole of VI, 2.02.

2-Phenylnaphthalene-1,2'-dicarboxylic Acid (Labeled VII). 1. By the Method of Graebe and Gnehm.[7]—The oxime of VI was prepared by an improved method from 3.0 g. of quinone VI, 1 g. of hydroxylamine hydrochloride, 15 ml. of ethanol and 2 ml. of pyridine. The product weighed 3.09 g. (96% of theory), m.p. 165–166° (cor.) (lit. (ref. 6, p. 273), 160–161°). Several preparations gave similar yields of 91–98%. The Beckmann rearrangement[7] of 4.50 g. of this oxime produced 2.81 g. (58.5% of theory) of mixed amido acids. Although Graebe and Gnehm[7] reported yields higher than 80%, we were unable to duplicate their yields. The alkaline hydrolysis[7] of the mixed amido acids was unsuccessful in our hands, since complete deamination was never achieved. An acid hydrolysis was therefore used which, although wasteful of material, yielded consistent amounts of purified dicarboxylic acid. In a typical run, 2.06 g. of product from the Beckmann rearrangement of the oxime of VI, 60 ml. of acetic acid and 15 ml. of hydrochloric acid were placed in a Pyrex tube. The tube was then sealed under vacuum (while the reaction mixture was frozen), and next placed in an oven for 6 hours at 150°. After cooling, the contents of the tube were concentrated to dryness in an air stream. From the solid product, 436 mg. of the ketone XIIIa (26.8%) was obtained (m.p. 131–133°), as bicarbonate-insoluble fraction. From the acidified bicarbonate solution by a continuous ether extraction a first crop of 932 mg. (45.5%) of the dicarboxylic acid VII was obtained by boiling off the ether and adding successive portions of benzene and petroleum ether (20–40°). A second crop of 409 mg. (24%) was obtained from the mother liquors. The total yield of acid VII was therefore 70%, and 96% of the starting material was accounted for. An analytical sample of VII, pre-

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(9) M. Orchin and L. Reggel, This Journal, **73**, 436 (1951). These authors kindly supplied us with their experimental procedure prior to publication of their paper.

(10) E. R. Alexander and A. C. Cope, *ibid.*, **66**, 888, footnote 7 (1944).

(11) M. Orchin and R. A. Friedel, *ibid.*, **71**, 3004 (1949).

(12) In several earlier radioactive carbonations, in which the carbon-C^{14} dioxide was in at least a onefold excess over 11H-benzo[a]fluorene-11-sodium, the molar radioactivity of acid II was lower by several per cent. than that of the carbon-C^{14} dioxide. It has now been shown that this difference in molar radioactivities is caused by the different rates of reaction of carbon-C^{12} dioxide and carbon-C^{14} dioxide with the organometallic reagent, and represents a true isotope effect (D. E. Pearson, B. M. Benjamin and C. J. Collins, unpublished work.)

(13) L. Fieser, M. Fieser and E. B. Hershberg, This Journal, **58**, 1463 (1936).

(14) R. H. Mayor and C. J. Collins, *ibid.*, **73**, 471 (1951), have described the application of this method to chrysene-5,6-C$_1^{14}$. In the discussion of the double-dilution method, the fact was overlooked that K. Bloch and H. S. Anker, *Science*, **107**, 228 (1948), had already pointed out the theoretical utility of this method.

pared by two crystallizations from ethanol-water, had a m.p. of 209.4–210.4° (cor.) (lit.[7] 199°). When the acid hydrolysis was carried out at 200° the yield of ketone XIIIa was quantitative, and no dicarboxylic acid VII was isolated. Since these particular samples were prepared from one of the earlier radioactive chrysenequinone preparations, their molar radioactivities (2.19 microcuries for VII and 1.41 microcuries for XIIIa) will not be consistent with those of the other compounds in the series VI → XIII.

2. **By Oxidation with Hydrogen Peroxide.**—To 9.61 g. (37.2 mmoles) of the quinone VI in 700 ml. of acetic acid was added 30 ml. of 30% hydrogen peroxide in three 10-ml. portions. Two portions were added all at once to the refluxing mixture at one-hour intervals and boiling was continued for one hour after the last portion of peroxide had been added. The cooled mixture was then allowed to cool and stand overnight. The last portion of peroxide was added the next day and boiling was continued for one hour. The cooled mixture was poured into an excess of water and the solid material was collected on a filter. This solid was digested in 5% sodium carbonate. From the filtrate was obtained 5.3 g. (18.1 mmoles, 49%) of crude dicarboxylic acid VII. The crude product did not exhibit a good melting point, and was not easily purified. Only after repeated treatment of aqueous alkaline solutions of the acid with charcoal, followed by filtration, acidification and filtration, with intermediate crystallizations from chloroform and methanol-water, was a pure sample obtained; m.p. 209.4–210.4°. The crude product, although probably containing large amounts of impurities, could be used directly for the cyclization with sulfuric acid, for the products (keto acids VIII and XI) were easily separated from the contaminants.

Cyclization of Labeled 2-Phenylnaphthalene-1,2′-dicarboxylic Acid (VII) to the Mixture of Keto Acids VIII and XI.—Following the procedure of Graebe and Gnehm,[7] 4.19 g. (14.4 mmoles) of crude VII and 33 ml. of concd. sulfuric acid yielded 1.93 g. (7.05 mmoles, 49%) of mixed keto acids VIII and XI. (When pure samples of VII were cyclized, the yields were sometimes as high as 75%, with an additional 15% of material being accounted for as the ketone XIII.) Varying quantities of a bicarbonate-insoluble fraction (chiefly XIII) were always obtained.

11H-Benzo[b]fluorene-11-one-5-carboxylic Acid (VIII, Labeled).—To the 1.93 g. of mixed acids obtained from the sulfuric acid-cyclization, was added a cooled solution of 1 ml. of acetyl chloride in 175 ml. of methanol. This mixture was boiled with refluxing for 24 hours. The solvent was removed in an air stream. An ether solution of the residue was extracted several times with aqueous sodium bicarbonate solution. This ether solution contained the methyl ester XII, and was treated as described in the next experimental section. From the acidified bicarbonate extracts 1.06 g. of a crude acid VIII was obtained. This material contained impurities (probably sulfonic acids), which were very tenacious and which were not removed even after repeated crystallization of the product. The purification was finally carried out by conversion of VIII to its methyl ester followed by hydrolysis back to the acid. Thus, the 1.06 g. of crude VIII was heated under reflux with 20 ml. of benzene and 2 ml. of thionyl chloride for two hours. The solution was taken to dryness, and to the solid residue was added 20 ml. of methanol and 0.5 ml. of pyridine. After the solution was heated under reflux for 1.5 hours it was concentrated to dryness. An ether solution of the residue was extracted several times with aqueous sodium carbonate solution. After the ether had been evaporated, 1.01 g. (3.51 mmoles, 50%) of the ester IX was obtained, m.p. 155–156° after crystallization from methanol–water.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.17; H, 4.17. Found: C, 79.32; H, 4.19.

For the ester hydrolysis, 0.760 g. of IX was boiled under reflux for 24 hours with 3 g. of sodium hydroxide in 60 ml. of methanol and 15 ml. of water. The solution was then concentrated nearly to dryness and acidified with excess dilute hydrochloric acid. The solid product VIII weighed 0.54 g., m.p. 255–256° (after crystallization from acetone–water or acetic acid).

Anal. Calcd. for $C_{18}H_{10}O_3$: C, 78.83; H, 3.65. Found: C, 78.89; H, 3.75; microcuries of carbon-14 per millimole of VIII, 2.04.

11H-Benzo[a]fluorene-11-one-7-carboxylic Acid (XI Labeled).—The ether solution from the methanol–acetyl chloride esterification (previous section) was concentrated, yielding 0.910 g. (3.16 mmoles, 45%) of the methyl ester XII, m.p. 169–173°. Crystallization from methanol–water produced orange needles, m.p. 175–176°.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.17; H, 4.17. Found: C, 79.20; H, 4.27; microcuries of carbon-14 per millimole of XII, 2.03.

The free acid XI was obtained by hydrolysis of 0.660 g. (2.29 mmoles) of XII by boiling the methyl ester for 24 hours in a solution of 3 g. of sodium hydroxide in 60 ml. of methanol and 15 ml. of water. The solution was evaporated nearly to dryness, and acidified with dilute hydrochloric acid. The solid residue when collected on a filter and dried weighed 0.473 g. An analytical sample of XI was prepared by crystallization of this material several times from acetic acid; m.p. 283–284° (lit.[7] 283°).

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 78.83; H, 3.65. Found: C, 78.82; H, 3.53; microcuries of carbon-14 per millimole of XI, 2.08.

11H-Benzo[b]fluorene-11-one-10,10a,11-C_1^{14} (X).—A mixture of 326 mg. of keto acid VIII, 10 ml. of quinoline and 20 mg. of copper chromite catalyst was heated at 250° in a Woods' metal-bath. The apparatus was so designed that a continuous nitrogen sweep led the evolved carbon-C^{14} dioxide into a bubbler filled with half-saturated barium hydroxide. Although no evolution of carbon-C^{14} dioxide was noticed during the first 15 minutes, the reaction was complete in 35 minutes. The filtered reaction mixture was taken to dryness and the solid residue of 232 mg. (84%) was crystallized. The yield of pure 11H-benzo[b]fluorene-11-one-10,10a, 11-C_1^{14} (X) was 188 mg. (73%); m.p. 156–157° (lit.[15] 155–156°).

Anal. Microcuries of carbon-14 per millimole of X, 1.27.

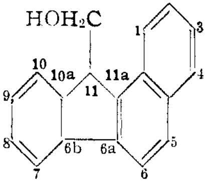
11H-Benzo[a]fluorene-11-one-5,6,11-C_1^{14} (XIII).—This ketone was prepared from the keto acid XI by a method analogous with that employed for the preparation of X. Thus 225 mg. of 11H-benzo[a]fluorene-11-one-7-carboxylic-5,6,11,*carboxy*-C_1^{14} acid (XI) yielded 48 mg. (26%) of purified 11H-benzo[a]fluorene-11-one-5,6,11-C_1^{14} (XIII); m.p. 135–136° (lit.[9] 134.5–135°). An additional 124 mg. of XIII was also obtained from the mother liquors.

Anal. Microcuries of carbon-14 per millimole of XIII, 1.80.

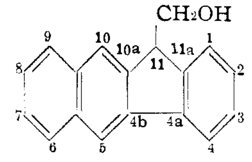
Analytical Determinations.[1]—Carbon-14 determinations for radioactive samples were carried out by burning the samples to carbon-C^{14} dioxide, using either wet or dry combustion methods, and determining the ion currents produced in the carbon-C^{14} dioxide samples in standard chambers with a vibrating reed dynamic condenser electrometer. Carbon and hydrogen analyses were performed by Dr. H. W. Galbraith, Knoxville, Tennessee.

Discussion of Results

A qualitative explanation can be proposed for the observation that 11H-benzo[a]fluorene-11-methanol-C^{14} (IV) rearranges on dehydration to yield 76% chrysene-5-C^{14} (Va) and 24% chrysene-6-C^{14} (Vb), while 11H-benzo[b]fluorene-11-methanol[14] (XIV) yields nearly equal amounts of the 5 (48%) and 6 (52%) labeled benz[a]anthracenes (XVb and XVa, respectively).[1b]



Numbering pattern of 11H-benzo[a]fluorene-11-methanol (IV)



Numbering pattern of 11H-benzo[b]fluorene-11-methanol (XIV)

The greater rate of reactivity of the α-position of naphthalene relative to the β-position is well

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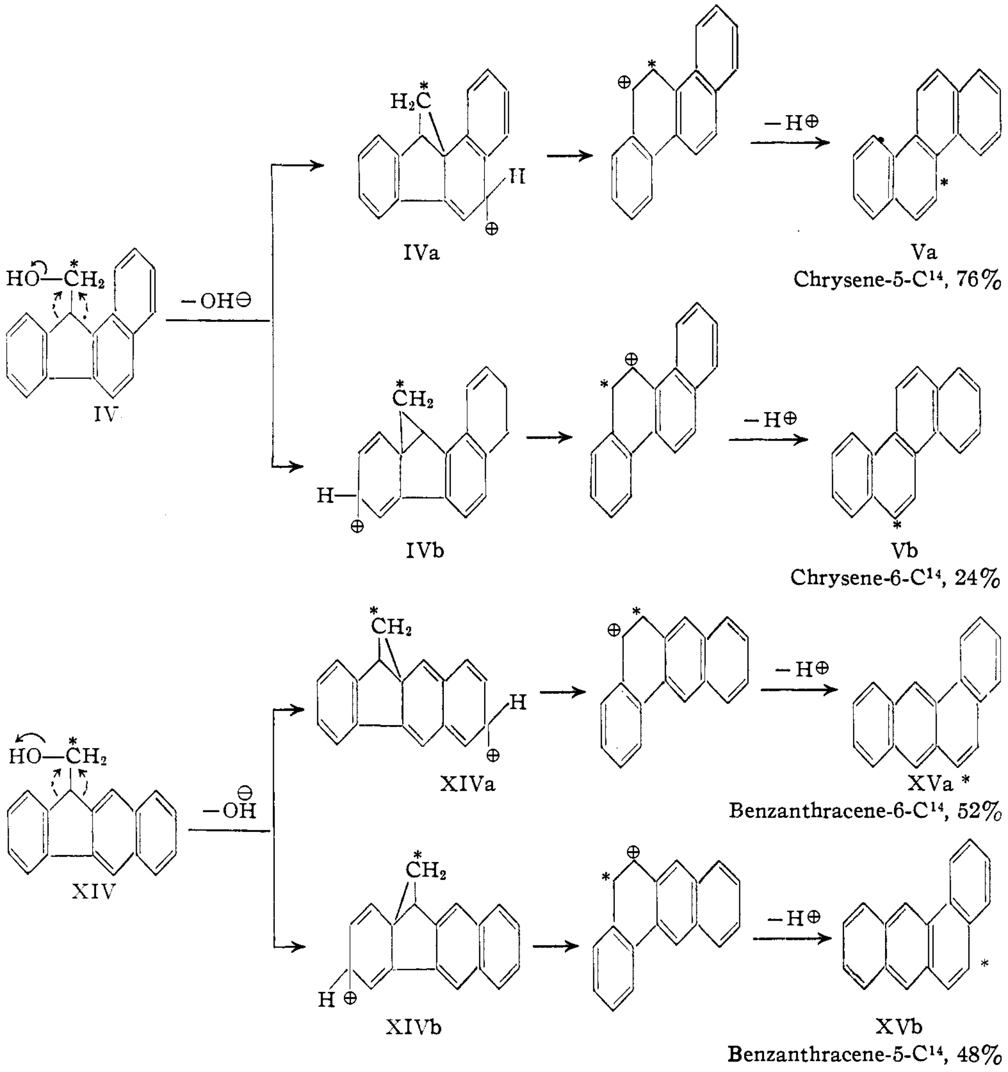
[15] J. Thiele and A. Wanschiedt. *Ann.*, **376**, 269 (1921).



known for aromatic substitution, and has been theoretically justified by Wheland.[16] Since during rearrangement of IV a substituted α-naphthyl position (11a) is competing for the carbinol carbon with a substituted phenyl position (10a) while in carbinol XIV the competing substituted positions are β-naphthyl (10a) and phenyl (11a), the observation that there is more chrysene-5-C^{14} (Va, α-naphthyl migration) in V than benz[a]anthracene-6-C^{14} (XVb, β-naphthyl migration) in XV might have been considered in fact a sound prediction. By further analogical reasoning it might have been predicted that chrysene-5-C^{14} (Va, α-naphthyl migration) should predominate over chrysene-6-C^{14} (Vb, o-phenyl migration) in the mixture V.

In the absence of relative rate data it is not possible to say decisively whether the migrating groups participate in the rate-determining removal of hydroxyl ion.[17] The resonance stabilized intermediates represented by the single typical structures IVa and IVb, and XIVa and XIVb however are consistent with the observed facts. The basic difference between these structures and those proposed by Cram[15] lies in the fact that in IVa, IVb, XIVa and XIVb the participating groups are connected to each other by the biphenyl bond which is typical of the fluorene nucleus. From molecular models of carbinols IV and XIV it seems that instead of preventing participation of the phenyl and naphthyl fragments during the dehydration–rearrangement process, the biphenyl bonds connecting the 6a–6b carbons in IV and the 4a–4b carbons in XIV in reality hold the phenyl and naphthyl fragments of these carbinols in nearly the optimum configuration necessary for participation in the rate-determing step.[18]

From molecular models of structure IV it may be inferred that the carbon and hydrogen atoms at the 1-position in this molecule exert either a negligible or a small steric effect on the course of the rearrangement, since there appears to be no more hindrance between the hydrogen at the 1-position and the hydroxyl group than between the hydrogen at the 10-position and the hydroxyl group.

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[16] G. W. Wheland, THIS JOURNAL, **64**, 900 (1942).

[17] "Participation" is used here to denote a simultaneous mechanism in which the migrating aryl group "pushes" while the dehydrating catalyst "pulls" hydroxyl ion from the carbinol. *Cf.* D. J. Cram, *ibid.*, **71**, 3863 (1949); S. Winstein and L. L. Ingraham, *ibid.*, **74**, 1160 (1952), and previous papers.

[18] This is particularly true if the non-planar structure for fluorene derivatives suggested by E. D. Hughes, C. G. LeFevre and R. J. W. Le Fevre (*J. Chem. Soc.*, 202 (1937)) and by J. Iball (*Z. Krist.*, **94**, 397 (1936)) can be assumed by carbinol IV.

The question of neighboring group participation in the Wagner rearrangement of 9-fluorenylcarbinols, and the steric effect owing to substitution at the 1-position of these carbinols will be the subject of future reports.

Acknowledgment.—The authors are indebted to Dr. J. D. Roberts and to Dr. W. M. Lauer for many valuable suggestions during the course of this work.

OAK RIDGE, TENNESSEE

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

Studies in the Wagner Rearrangement.[1-3] IV. The Steric Effect of an Ortho Methyl Group

BY BEN M. BENJAMIN[4] AND CLAIR J. COLLINS

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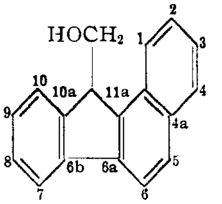
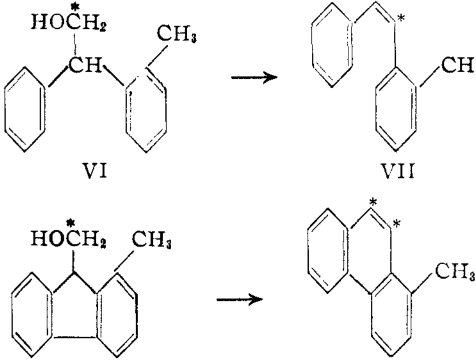
2-Phenyl-2-(*o*-tolyl)-ethanol-1-C^{14} (VI) and 1-methyl-9-fluorenyl-(carbinol-C^{14}) (XIV) have been converted by the Wagner rearrangement to labeled *o*-methylstilbene (VII) and labeled 1-methylphenanthrene (XV), respectively. Chemical degradation of the *o*-methylstilbene (VII) indicated that the phenyl group of VI had migrated in preference to the *o*-tolyl group in the ratio 55:45. Degradation of the labeled 1-methylphenanthrene (XV) showed that the phenylene and *o*-tolylene fragments of XIV had migrated in the ratio 50:50. These results show that although the methyl group of VI exerts a small steric effect during rearrangement, the methyl group in 1-methyl-9-fluorenylcarbinol exerts a negligible over-all effect on the dehydration–rearrangement of this latter compound.

Introduction

In prior papers[1] syntheses of carbon-labeled phenanthrene, benz[a]anthracene and chrysene through the dehydration–rearrangements of substituted 9-fluorenylcarbinols have been reported. While the carbon-14 was nearly equally distributed between the two labeled positions of benz[a]anthracene, it was distributed between the 5- and 6-positions of chrysene in the ratio of 76:24. It was suggested[1c] that the carbon and hydrogen in the 1-position of 11H-benzo[a]fluorene-11-methanol exert little if any steric influence during the rearrangement of this carbinol. It was of interest therefore to study the Wagner rearrangement of 1-methyl-9-fluorenylcarbinol (XIV), since from molecular models of XIV there is indicated very little hindrance between the methyl and carbinol groups of this compound. In 2-phenyl-2-(*o*-tolyl)-ethanol (VI) however, the methyl group should be free to exert its steric hindrance to *o*-tolyl migration by limiting rotation about the bond connecting the tolyl group with the tertiary carbon, and thus limiting the probability of orientations favorable to *o*-tolyl group migration. While it is in fact probable that there is a steric interaction between the *o*-tolyl and phenyl groups of compound VI owing to the methyl residue, it seems unlikely that the mobility of the phenyl group is affected to exactly the same degree as that of the *o*-tolyl group.



11H-Benzol[a]fluorene-11-methanol



If these postulates are true, then the phenyl group of carbinol VI should migrate with higher frequency than the phenylene group of carbinol XIV during the Wagner rearrangements of these compounds. A comparison of the carbon-14 distributions in the products VII and XV, obtained from the labeled carbinols VI and XIV, respectively, should therefore permit a qualitative test of our hypothesis.

Rearrangement of 2-Phenyl-2-(*o*-tolyl)-ethanol-1-C^{14} (VI).—2-Phenyl-2-(*o*-tolyl)-ethanol-1-C^{14} (VI) was prepared by the general procedure of Burr and Ciereszko.[5] The synthesis of this carbinol, its rearrangement to labeled *o*-methylstilbene (VII), and the degradative procedure used to locate the radioactivity in the latter compound are shown in the reaction series IV → X inclusive. Each labeled position is indicated by the asterisk (*). Radioactivities are shown under the appropriate structures and are expressed as microcuries of carbon-14 per millimole (μc./mmole). From the millimolar ra-

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(1) Previous papers: (a) I, C. J. Collins, THIS JOURNAL, **70**, 2418 (1948); (b) II, C. J. Collins, J. G. Burr and D. N. Hess, *ibid.*, **73**, 5176 (1951); (c) III, C. J. Collins, D. N. Hess, R. H. Mayor, G. M. Toffel and A. R. Jones, *ibid.*, **75**, 397 (1953).

(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) From the Ph.D. Thesis of Ben M. Benjamin.

(4) Graduate Fellow from the University of Florida, Gainesville, Florida. Fellowship sponsored jointly by the Oak Ridge Institute of Nuclear Studies and the Oak Ridge National Laboratory.

(5) Drs. J. G. Burr, Jr., and L. Ciereszko, in this Laboratory, have prepared a series of unsymmetrically meta- and para-substituted 2,2-diphenylethanols.