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A STUDY OF THE ISOMERIZATION OF C14-LABELED PERINAPHTHENE

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A STUDY

PERINAPHTHENE OF C-14

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Masao Nakazaki

March 28, 1957

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Radiation Laboratory and Department of Chemistry  
University of California, Berkeley, California

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ABSTRACT

Perinaphthene labeled at the number 8 position with C<sup>14</sup> has been synthesized. Upon a variety of oxidative degradations it has been shown that the perinaphthene molecule behaves as though it were in a rapid tautomerism, so that positions 2 and 5 are equivalent to position 8.

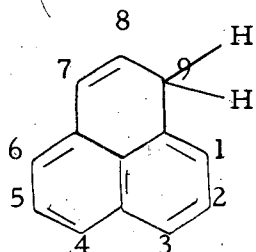
A STUDY OF THE ISOMERIZATION OF C<sup>14</sup>-LABELED PERINAPHTHENE\*

Masao Nakazaki†

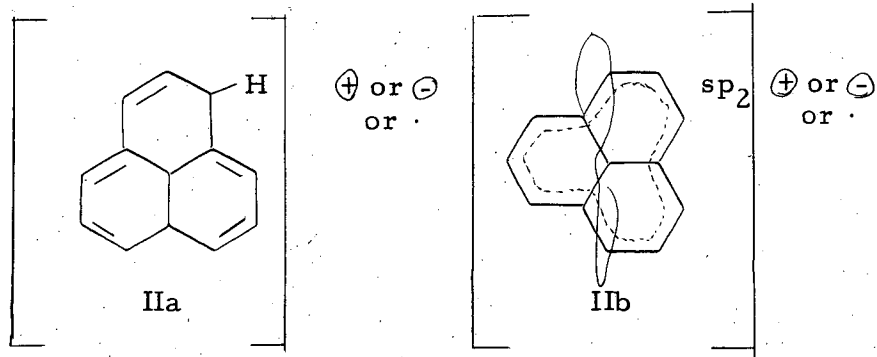
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Perinaphthene (I) is an especially interesting compound. If one hydrogen atom at position 7 is removed by any means, the resulting perinaphthyl group (cation, anion, or free radical) should have the completely symmetrical, stable resonance structure IIa or IIb.



(remove H<sup>+</sup> or H<sup>-</sup> or H·) →



The situation is analogous to the relationship between triphenylmethane and triphenylmethyl radical (cation, anion, or free radical).

The first research work along this line was that by Robinson and Klyne,<sup>1</sup> who suggested the existence of tautomerism in alkyl perinaphthene, i. e., the possible existence of six forms, corresponding to the six positions

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<sup>1</sup>W. Klyne and R. Robinson, J. Chem. Soc. 1938, 1991.

available for the "extra" hydrogen on the nucleus. These workers attempted the synthesis of 1-methylperinaphthene to prove this assumption. If sixfold tautomerism occurred, the oxidation product might be a mixture of three dicarboxylic acid anhydrides: naphthalic anhydride, 1-methylnaphthalic anhydride, and 3-methylnaphthalic anhydride. However, their attempts to prepare this compound were unsuccessful.

The first instance of isomerization in the perinaphthene series of the type discussed by Robinson and Klyne<sup>1</sup> was discovered by Fieser and Gates<sup>2</sup> when they reacted *o*-chlorophenylmagnesium bromide and perinaphthanone. After the reaction product was subjected to dehydration, hydrogenation, and cyanidation, they were able to get two isomeric cyanides; these were different at the positions of attachment of *o*-chlorophenyl groups at the 1 and 3 positions of the perinaphthene nucleus, respectively.

In 1950 Boekelheide and Larrabee<sup>3</sup> succeeded in preparing methylperinaphthene. They dehydrated four different types of methylperinaphthanol, which had methyl groups at the 1, 3, 7 and 9 positions, respectively. They obtained only one methylperinaphthene, to which they assigned the structure of 1-methylperinaphthene, mainly on the basis of the study of the dihydro-compound.<sup>4</sup> From the results of these experiments it is obvious that in at least three of these alcohols dehydration must be accompanied by isomerization. But in the case of methyl-substituted perinaphthene it is still conceivable that the double bond must be forced to move to the most stable fixed position governed by the inductive and hyperconjugation effect of the methyl group. Therefore, it seemed interesting to see whether or not the double bond would move in perinaphthene itself. In this paper, the synthesis of perinaphthene-8-C<sup>14</sup> is described, and the product of this synthesis was used to shed light on the mechanism of perinaphthene isomerization.

By the same procedure as used by Boekelheide and Larrabee,<sup>3</sup> C<sup>14</sup> labeled perinaphthene (VIII) with the C<sup>14</sup> in the 8-position was synthesized according to the scheme in Fig. 1. The location of C<sup>14</sup> in the 8 position in perinaphthanone-7 (IV) was ensured by selenium dioxide oxidation of the ketone in acetic acid and potassium permanganate oxidation of this product (V) to nonradioactive naphthalic anhydride (VI). Upon potassium permanganate

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<sup>2</sup>L. F. Fieser and M. D. Gates, *J. Am. Chem. Soc.* 62, 2335 (1940).

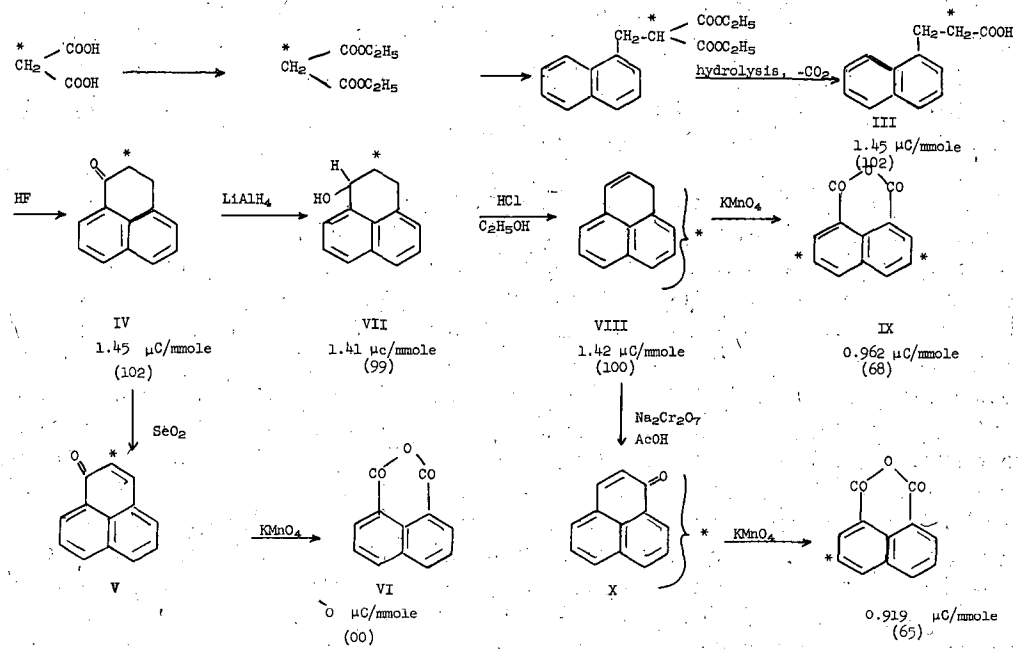
<sup>3a</sup>V. Boekelheide and C. E. Larrabee, *J. Am. Chem. Soc.* 72, 1240 (1950).

<sup>3b</sup>V. Boekelheide and C. E. Larrabee, *J. Am. Chem. Soc.* 72, 1245 (1950).

<sup>3c</sup>V. Boekelheide and M. Goldman, *J. Org. Chem.* 19, 575 (1954).

<sup>3d</sup>V. Boekelheide and M. Goldman, *J. Am. Chem. Soc.* 76, 604 (1954).

<sup>4</sup>There remains some doubt in this assignment of structure, because on a surface of a hydrogenation catalyst the migration of double bonds might occur. Concerning the discrepancy of the structure assignments between oxidative degradation and hydrogenation of 8-methylperinaphthene, see Reference 3c.



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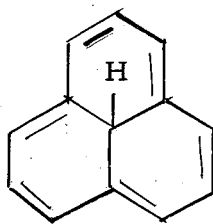
Fig. 1. Scheme for synthesis of perinaphthene labeled in the 8-position with  $C^{14}$ . The figures in parenthesis are the specific activities based on the specific activity (100) of perinaphthene (VIII.)



oxidation of the  $C^{14}$ -labeled perinaphthene (VIII) in acetone, the naphthalic anhydride (IX), which had almost two-thirds the specific activity of perinaphthene, was obtained.

In the case of permanganate oxidation in acetone, the reaction mixture became alkaline, so it is probable that there exists an equilibrium between the perinaphthene and its symmetrical anion (II a, b)<sup>5</sup> in which the 2, 5, and 8 positions are equivalent. In order to avoid such an equilibrium, sodium dichromate oxidation in acetic acid was also tried.

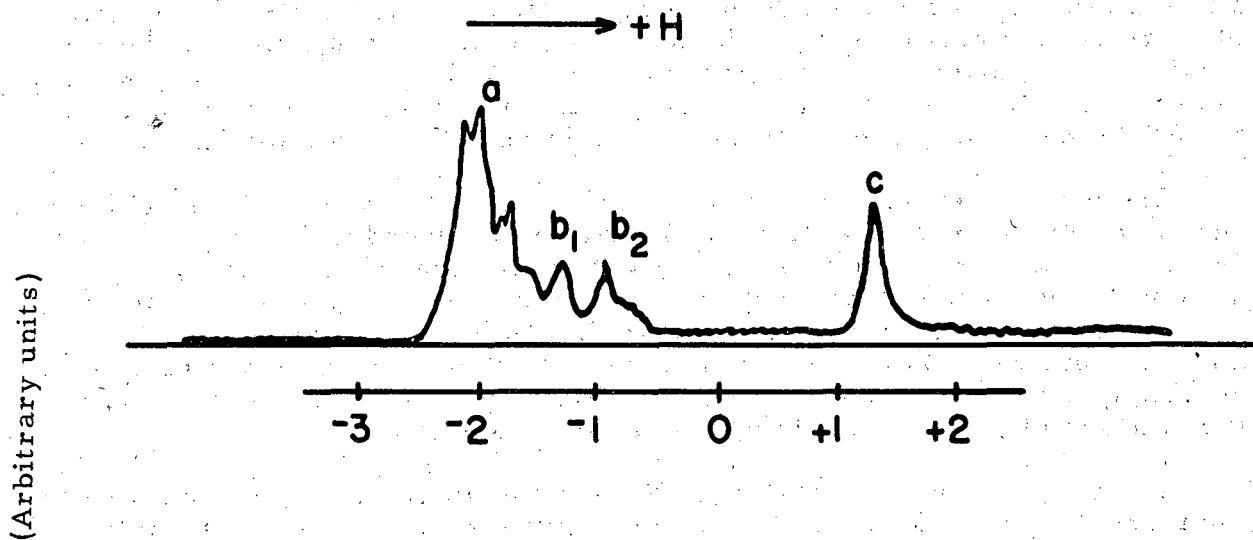
The intermediate perinaphthenone (X) was further oxidized with permanganate, and naphthalic anhydride (XI) was again obtained. This product was also found to have almost two-thirds the specific activity of the starting material. These results, which show that one-third of the  $C^{14}$  activity is lost in the oxidation stage, could be explained in one of the following ways: (1) The migration of the double bond occurs at the stage of dehydration of perinaphthanol (VII), so that the perinaphthene obtained could have  $C^{14}$  evenly distributed between the 2, 5, and 8 positions; (2) at the oxidation stage, the symmetrical intermediate (II a, b) (as cation or free radical) could exist; (3) perinaphthene could have a symmetrical structure (XII).<sup>6</sup> This third assumption can be rejected on the basis of the observation of its nuclear magnetic resonance spectrum, in which there are found four peaks, a, b<sub>1</sub>, b<sub>2</sub>, and c (Fig. 2). Their ratio of intensity was found to be approximately 6:1:1:2, which coincides exactly with the structure of I (6 aromatic protons, 2 ethylenic protons, and 2 methylene protons, with the 2 ethylenic protons in dissimilar environments).



XII

<sup>5</sup>The acidity of perinaphthene is between that of triphenylmethane and cyclopentadiene. See Reference 3b.

<sup>6</sup>The ultraviolet spectrum of perinaphthene shows some peculiarity (see Fig. 3) in comparison with the one of 1-( $\alpha$ -naphthyl)-propene-1, max. 292 m $\mu$  (log  $\Sigma$  4.0); cf. M. Petersen and F. Manchen, *Monatsh. Chem.* **68**, 97 (1936).



**Perinaphthene in CCl<sub>4</sub>**

MU-12603

Displacement from water (gauss)

Fig. 2. Proton nuclear magnetic resonance of perinaphthene in carbon tetrachloride (33 mg/0.3 ml). Zero point is the position of proton of water. The relative areas under the peaks a, b<sub>1</sub>, b<sub>2</sub>, and c are 164, 30, 28, and 50; the ratio is approximately 6:1:1:2.

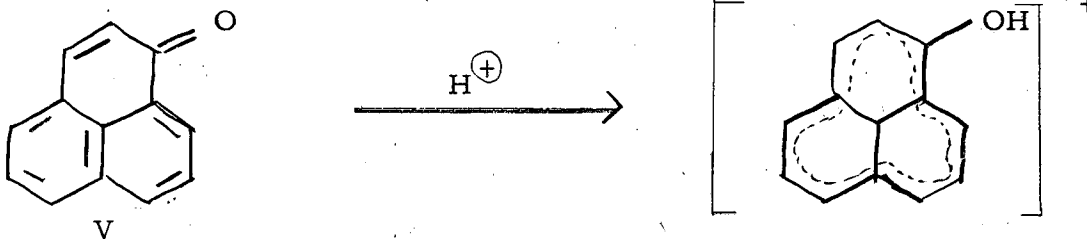
Assumptions (1) and (2) above cannot be distinguished on the basis of the work performed with carbon-14. Fieser and Gates<sup>2</sup> suggested that the isomerization occurs at the dehydration stage of the alcohol, and Boekelheide and Larrabee<sup>7</sup> proposed a mechanism in which they suggested the addition of a proton to a double bond in the naphthalene nucleus followed by the migration of the double bond into the third ring, and, finally, detachment of the proton. As a result of their work on the migration of double bonds in the methylperinaphthalene series, Assumption (1) seems most likely.

The ultraviolet spectrum of perinaphthene in ethanol-hydrogen chloride, which has the same concentration as obtained by dehydration of the alcohol (VII), was the same as that of perinaphthene in ethanol (Fig. 3a). However, a tremendous change in the spectrum was found in the solution of trifluoroacetic acid (Fig. 3c.), which suggests that there exists some form of an addition compound of a proton and this hydrocarbon.<sup>8</sup> By means of optical density measurement, about 85% of the perinaphthene was recovered after the solution of trifluoroacetic acid was put into ethanol.

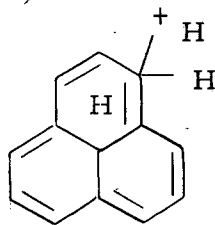
One of the possible structures (XIV) of the addition product is interesting from the point of view of its symmetrical structure, which is a fully aromatic complex system.<sup>9</sup>

<sup>7</sup>See the footnote in Reference 3a.

<sup>8</sup>L. J. Andrews, Chem. Rev. 54, 713 (1954). It seems very interesting to compare the change of ultraviolet spectrum of perinaphthenone (V) in trifluoroacetic acid (Figs. 3d and 3e).



<sup>9</sup>A somewhat different structure for the salt of perinaphthene has been suggested by Clar.<sup>10</sup>



<sup>10</sup>E. Clar, Aromatisch Kohlenwasserstoffe (Springer-Verlag, Berlin, 1952), p. 432.

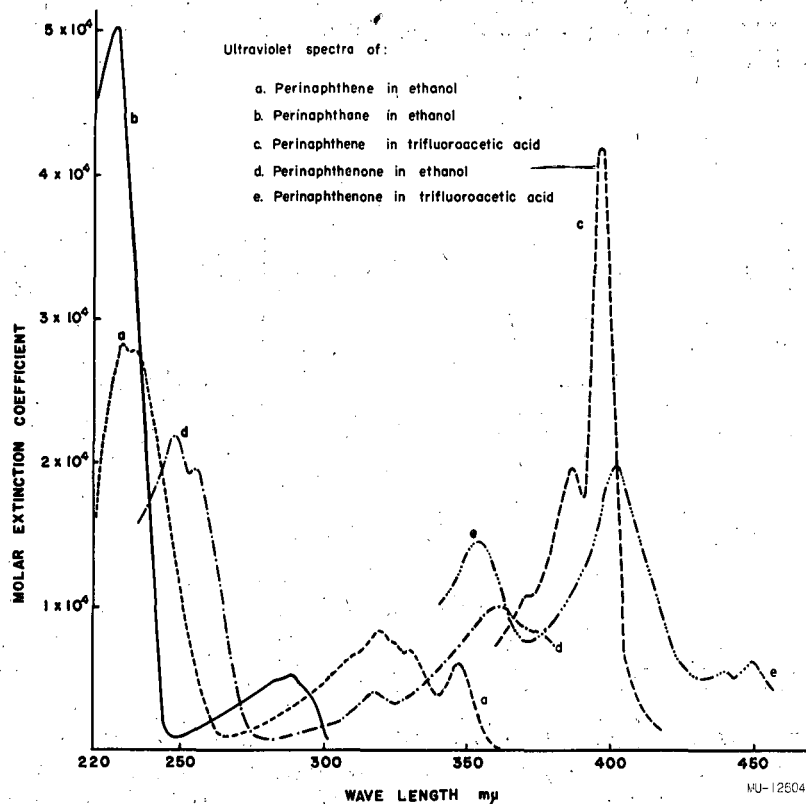
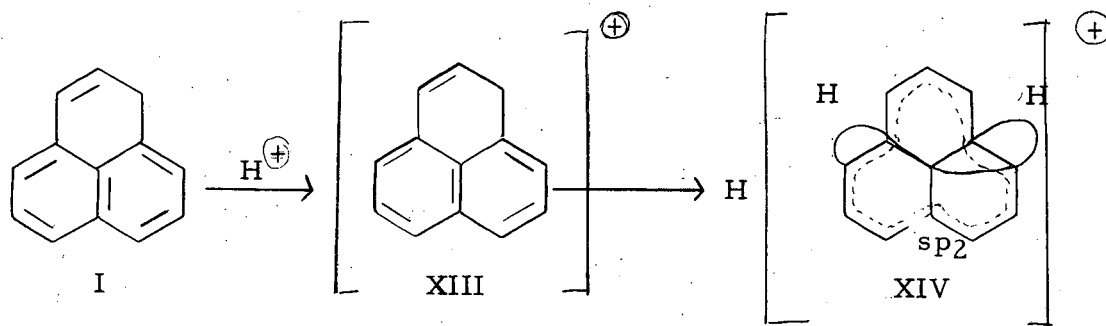


Fig. 3. Ultraviolet spectra of

- a. Perinaphthene in ethanol: 230  $m\mu$  ( $2.82 \times 10^4$ );  
235  $m\mu$  ( $2.80 \times 10^4$ ); 319  $m\mu$  ( $8.29 \times 10^3$ ); 348  $m\mu$  ( $6.08 \times 10^3$ ).
- b. Perinaphthene in ethanol: 228  $m\mu$  ( $5 \times 10^4$ ); 288  $m\mu$  ( $5 \times 10^3$ ).  
See Boekelheide and Larrabee<sup>3b</sup>.
- c. Perinaphthene in trifluoroacetic acid; 371  $m\mu$  ( $1.09 \times 10^4$ );  
387  $m\mu$  ( $1.97 \times 10^4$ ); 396  $m\mu$  ( $4.19 \times 10^4$ ).
- d. Perinaphthenone in ethanol; 248  $m\mu$  ( $2.18 \times 10^4$ ); 256  $m\mu$  ( $1.97 \times 10^4$ );  
317  $m\mu$  ( $3.99 \times 10^3$ ); 361  $m\mu$  ( $1.03 \times 10^4$ ).
- e. Perinaphthenone in trifluoroacetic acid: 354  $m\mu$  ( $1.47 \times 10^4$ );  
402  $m\mu$  ( $1.98 \times 10^4$ ).

The existence of the perinaphthene proton complex suggests that this complex might be the intermediate in isomerization. The completely symmetrical structure of the perinaphthyl free radical (II b), which is expected in view of the theory of resonance, was definitely proved by the observation of the electron spin resonance spectrum of perinaphthene in carbon tetrachloride.<sup>11</sup>



### EXPERIMENTAL<sup>12</sup>

#### Diethyl $\alpha$ -naphthylmethyl malonate-2-C<sup>14</sup>

Ten ml of an ether solution of diazoethane<sup>13</sup> prepared from 700 mg of N-nitrosoethylurea was poured onto a mixture of about 10 mg of malonic-2-C<sup>14</sup> acid having a specific activity of approximately 9.6 uC/mg,<sup>14</sup> and 68 of

<sup>11</sup>Sogo, Nakazaki, and Calvin, J. Chem. Phys., in press.

<sup>12</sup>All analyses were performed by the Microanalytical Laboratory, Department of Chemistry and Chemical Engineering, University of California, Berkeley. All melting points were uncorrected. Ultraviolet spectra were determined on a Cary recording spectrophotometer, Model 14. Nuclear magnetic resonance measurements were performed on a Varian Model 4300B spectrometer.

Radioactivity determinations were performed by Mr. Irville Whittemore of the Bio-Organic Chemistry Group of the Radiation Laboratory, using the ionization chamber method of K. E. Wilzbach and W. Y. Sykes, Science 120, 494 (1954).

<sup>13</sup>Prepared according to the procedure for diazomethane outlined in Organic Syntheses, Coll. Vol. II, (Wiley, New York, 1947), p. 461, using ethylamine hydrochloride instead of methylamine solution. Also cf. Organic Syntheses, Coll. Vol. II, p. 165.

<sup>14</sup>Obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee.

nonradioactive malonic acid. After the resulting mixture had stood for 4 hr at room temperature, the solvent was evaporated on a steam bath under a nitrogen stream. One ml of benzene was added to the oily residue, and the solution evaporated to remove traces of water in the azeotrope. Nonradioactive diethyl malonate was added to bring the total weight of the ester to 3.283 g.

To the warm solution of sodium isopropylate in isopropanol, which was prepared by dissolving 0.407 g (0.017 mole) of sodium in 20 ml of isopropanol, was added at once 3.283 g of  $C^{14}$ -labeled diethyl malonate in 10 ml of isopropanol, and with stirring and gentle boiling the solution of  $\alpha$ -chloromethylnaphthalene (3.012 g, 0.017 mole) in 20 ml of isopropanol was added over a period of 6 hr. Stirring and boiling were continued for another 8 hr, and 30 ml of isopropanol was distilled off.

The straw-yellow residue was poured onto 20 g of crushed ice and acidified by the addition of 2 N hydrochloric acid, followed by extraction with ether. The ether extract was washed successively with 5% sodium carbonate, water, and saturated aqueous sodium chloride. After drying with anhydrous magnesium sulfate, the ether was removed and the product was fractionated under 1.5 mm Hg. After recovery of 1.113 g of diethyl malonate (bp 57-59°), diethyl  $\alpha$ -naphthylmethyl malonate was distilled as a colorless viscous oil, bp 177°. Yield: 3.382 g (66% based on chloride).

#### $\beta$ -(1-Naphthyl)-propionic acid

The mixture of 3.382 g of the  $\alpha$ -naphthylmethyl malonate, dissolved in 5 ml of methanol and 10 ml of 6 N sodium hydroxide, was refluxed for 3 hr, after which another 2 ml of 6 N sodium hydroxide was added and refluxing was continued for another hour. After the evaporation of the methanol on a steam bath under a nitrogen stream, the solution of the hydrolyzate was neutralized by the addition of 6 N hydrochloric acid. A clear boiling solution resulted from the addition of 50 mg of Norite and filtration with the aid of Celite. The solution was acidified carefully in order to precipitate the malonic acid. After filtration, washing, and drying, this material weighed 2.222 g (81% yield).

Decarboxylation of the substituted malonic acid (2.222 g) started at 163° (bath temperature) and was completed by heating at 176° for one-half hour. The substituted propionic acid (1.833 g, mp 154-156.5°) was recrystallized from carbon tetrachloride, mp, 156-157°. Yield: 1.727 g. (Fieser and Gates<sup>2</sup> reported a mp of 156-156.7° from benzene-methanol.) A second crop (0.05 g) with a mp of 154-156° was obtained from the mother liquor. Total yield: 1.777 g (63.5%).

Anal. Calcd for  $C_{13}H_{12}O_2$ : C, 77.98; H, 6.04. Found: C, 77.79; H, 6.07. Specific activity: 1.45  $\mu C$ /mmole.

#### Perinaphthanone-7, 8- $C^{14}$

The mixture of 1.777 g of  $\beta$ -(1-naphthyl)-propionic acid and 5 g of liquid hydrogen fluoride in a polyethylene bottle was placed in a hood for 2 hr. Two hundred g of crushed ice was added to the red reaction mixture,

and the yellow solid that precipitated was extracted with ether. The ether solution was extracted with 10% sodium carbonate solution to remove unreacted acid, then was washed with water and saturated sodium chloride solution. The neutral fraction (1.505 g, 94%), after being dried over anhydrous magnesium sulfate and removed from the solvent, was dissolved in a mixture of 70 ml of n-hexane and 2 ml of benzene and passed through an 8-by-150-mm alumina column<sup>15, 16</sup> Upon elution with n-hexane followed by n-hexane-benzene, perinaphthanone (0.771 g) was obtained after the evaporation of the solvent and recrystallization from n-hexane. Faintly yellow prisms were obtained, mp 80-80.5° (Fieser and Gates<sup>2</sup> reported mp 82.6-83.2°), by further adsorptive purification and by several recrystallizations from benzene-hexane. A second crop (0.139 g) melting at 75-77° was obtained from the mother liquor. The total yield of perinaphthanone sufficiently pure for use in the next step was 0.910 g (62%).

Anal. Calcd for C<sub>13</sub>H<sub>10</sub>O: C, 85.69; H, 5.53. Found: C, 85.78; H, 5.67. Specific activity: 1.45  $\mu$ C/mmole.

#### Degradation of perinaphthanone-7, 8-C<sup>14</sup>

To the mixture of 125 mg of perinaphthanone and 10 ml of acetic acid was added 43 mg of selenium dioxide (theor. 37 mg), and the solution was refluxed for 4 hr. The color of the mixture rapidly became red, and the gray precipitate of the selenium metal separated. The selenium was filtered off and washed with benzene. The combined acetic acid and benzene washings were evaporated under vacuum by water pump. The reddish-yellow residue was purified by sublimation under 1 mm Hg, with a bath temperature of 140°.

The bright yellow sublimate (96 mg, 77.5%)<sup>17</sup> was dissolved in 25 ml of acetone and oxidized by the addition to the mixture of 280 mg (theor. 277 mg) of potassium permanaganate and 30 ml of acetone over a period of 6 hr at room temperature. After standing overnight, the reaction mixture was evaporated to 5 ml, and 15 ml of water was added. The manganese dioxide suspension was put into solution by the addition of 6 N hydrochloric acid and warming on the steam bath.

The golden yellow fine needles that precipitated from the acidic solution were filtered and washed with water; yield, 92 mg. The crude naphthalic

<sup>15</sup>The alumina used in this experiment was "Aluminum Oxide, Woelm"; neutral (nonalkaline), activity Grade 1, obtainable from Alupharm Chemicals Co., 54 C St., Elmont, Long Island, New York.

<sup>16</sup>4, 5-Benzhydrindone-1 remained on the alumina; cf. Fieser and Gates.<sup>2</sup>

<sup>17</sup>In the cold run, this perinaphthenone was purified by recrystallization from ligroin (bp 65-110°) with small amount of benzene; mp 153-155°. Anal. Calcd for C<sub>13</sub>H<sub>8</sub>O: C, 86.65; H, 4.48. Found: C, 86.04; H, 4.58.

anhydride was purified as follows: The crystals were taken into solution by warming with 10 ml of 1 N sodium hydroxide, and decolorized with Norite. From the alkaline solution, naphthalic anhydride was reprecipitated with 6 N hydrochloric acid and filtered. After drying, this material weighed 86 mg, from which 70 mg was purified by sublimation at 1 mm Hg with a bath temperature of 140–190°, and the sublimate was recrystallized from ethanol with a small amount of acetone. Yield: 47 mg, mp 266–268°. (From the mother liquor an additional 18 mg was obtained; total yield, 48%).

Anal. Calcd for  $C_{12}H_6O_3$ : C, 72.73; H, 3.05. Found: C, 72.42; H, 3.08.  
Specific activity:  $0.2 \mu C/mmole$ .

#### Perinaphthanol-7, 8- $C^{14}$

To a stirred suspension of 61 mg of lithium aluminum hydride in 10 ml of ether was added a mixture of 802 mg of perinaphthanone, and 25 ml of ether was added at room temperature. The addition of the ketone was controlled by adding only enough to keep the ether boiling; this required about 10 min. After an additional 10 min of stirring, water was added, followed by the addition of 0.6 N hydrochloric acid to dissolve aluminum hydroxide. The reaction product was extracted with ether, and the ether extract was washed successively with water, 1% sodium bicarbonate, water, and saturated sodium chloride solution. The faintly yellow residue resulting from the evaporation of ether was solidified. Yield: 752 mg, mp 68–70°. Recrystallization from n-hexane gave a prismatic crystalline substance; 672 mg, mp 74–76°. From the mother liquor an additional 27 mg of product was obtained. Total yield 699 mg (84%).

Anal. Calcd for  $C_{13}H_{12}O$ : C, 84.75; H, 6.57. Found: C, 85.45; H, 6.47.  
Specific activity:  $1.41 \mu C/mmole$ .

#### $C^{14}$ -Labeled perinaphthene

To a mixture of 231 mg of perinaphthanol and 4 ml of absolute ethanol was added at 0° 4 ml of absolute ethanol saturated at 0° with hydrogen chloride. The solution was refluxed for 15 min. The color of the resulting solution was yellow, but an intense blue fluorescence was observed after a few minutes boiling.<sup>19</sup> The reaction mixture was placed in 150 g of

<sup>18</sup>Boekelheide and Larrabee<sup>3</sup> obtained the alcohol, mp 85°, but they did not try to purify this substance. In a cold run at this stage, the alcohol which had a mp of 84–85.5° was obtained, but recrystallization from n-hexane gave the prismatic crystalline substance, which had a mp of 79–80°. This material was observed to change its crystal form into a needlelike crystalline substance after standing a few days in a vial; the melting point was the same as the original prismatic crystal, however.

<sup>19</sup>Boekelheide and Larrabee<sup>3</sup> noticed that the color of the solution changed from orange to deep blue. They must have confused the color of the solution with the fluorescence.



crushed ice and extracted with n-pentane. This pentane extract was washed with water and dried with anhydrous magnesium sulfate. Evaporation of the solvent gave a yellow residue, which was dissolved in n-pentane and passed through an 8-by-150-mm alumina column followed by elution with n-pentane. After the evaporation of the n-pentane, 153 mg (73%) of perinaphthene<sub>3</sub> was obtained as colorless plates, mp 82-83.5°. (Boekelheide and Larrabee<sup>3</sup> report mp 85-86°.)

Anal. Calcd for C<sub>13</sub>H<sub>10</sub>: C, 93.94; H, 6.06. Found: C, 94.05; H, 5.93.  
Specific activity: 1.42 μC/mmole.

#### Oxidative Degradation of C<sup>14</sup>-labeled Perinaphthene

(a) Direct potassium permanganate oxidation. A mixture of 380 mg of potassium permanganate (theor. 385 mg) and 30 ml of acetone was added at room temperature over a period of 6 hr to a stirred solution of 86 mg of perinaphthene in acetone. The acetone was removed from the reaction mixture, leaving a volume of almost 5 ml, and 20 ml of water was added. The manganese dioxide suspension was dissolved by the addition of 200 ml of 3 N hydrochloric acid and the solution was warmed on a steam bath. The yellow, fine needle-like crystals were filtered, washed and dried. Yield: 81 mg (79.5%). The product was redissolved in 1 N sodium hydroxide solution by warming with Norite, and filtered with the aid of Celite.

To the clear alkaline solution, 6 N hydrochloric acid was added to reprecipitate the naphthalic anhydride, and the precipitated anhydride was washed with water and dried. Yield: 72 mg. After purification by sublimation at 1 mm Hg with a bath temperature of 150-180°, naphthalic anhydride (64 mg) was recrystallized from ethanol. Yield: 46 mg. An additional 6 mg of naphthalic anhydride was isolated from the mother liquor. Total yield, 51%; mp 264-266°.

Anal. Calcd for C<sub>12</sub>H<sub>6</sub>O<sub>3</sub>: C, 72.73; H, 3.05. Found: C, 71.92; H, 3.19.  
Specific activity: 0.96 μC/mmole.

(b) Combined oxidation with sodium dichromate and potassium permanganate. The mixture of 120 mg of perinaphthene and 3 ml of acetic acid was added to a solution of 936 mg of sodium dichromate in 8 ml of acetic acid and warmed on a steam bath for 1.5 hr. The reaction mixture was then poured onto 200 g of crushed ice and the yellow precipitate of perinaphthenone was filtered and washed with water. Yield: 91 mg (70%).

This perinaphthenone (91 mg) was dissolved in 25 ml of acetone and oxidized by the addition of 264 mg of potassium permanganate in 30 ml of acetone at room temperature over a period of 6 hr. The acetone was evaporated to a volume of 5 ml, and 20 ml of water was added. The manganese dioxide suspension was dissolved by warming on a steam bath with 15 ml of 3 N hydrochloric acid. The yellow crystals of naphthalic anhydride which separated were filtered, washed with water, and redissolved in 10 ml of 1 N sodium hydroxide. This alkaline solution was treated with Norite and filtered through a layer of Celite. The naphthalic anhydride, which was precipitated by addition of 6 N hydrochloric acid, weighed 62 mg.

This material was further purified by sublimation at 1 mm Hg with a bath temperature of 190°, and the sublimate was recrystallized from ethanol with small amounts of acetone. Yield: 56 mg, mp 264-267°. An additional 6 mg of naphthalic anhydride was obtained from the mother liquor, bringing the total yield to 43.3%.

Anal. Calcd for C<sub>12</sub>H<sub>6</sub>O<sub>3</sub>: C, 72.73; H, 3.05. Found: C, 71.88; H, 3.05.  
Specific activity: 0.92 μC/mmole.