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# THE SYNTHESIS OF 5,6,7,8-TETRAHYDRO-(5,8-$^3$H)NAPHTHALENE AND DECAHYDRO-(7-$^3$H)NAPHTHALENE BOTH LABELED WITH $^{14}$C IN THE 1- OR 2-POSITION*

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**Abstract**—Procedures are given for the preparation of (1-$^{14}$C),(5,8-$^3$H)tetralin,(2-$^{14}$C),(5,8-$^3$H)tetralin, (1-$^{14}$C),(7-$^3$H)decalin and (2-$^{14}$C),(7-$^3$H)decalin. Tetralin labeled with $^{14}$C in the aromatic ring was prepared from tetralol labeled with $^{14}$C in the aliphatic ring by conversion to naphthol and selective hydrogenation of the hydroxylated ring. Decalin specifically labeled with tritium was prepared by catalytic reduction of tritiated tetralin. The 1-$^{14}$C-labeled compounds were obtained from $^{14}CO_2$ in a 5- or 9-step synthesis with an overall yield of 35 and 25%, respectively, the 2-$^{14}$C-labeled compounds in a 9- or 13-step synthesis with an overall yield of 25 or 18%, respectively. The specificity of the $^{14}$C-labeling was in all cases better than 95%.

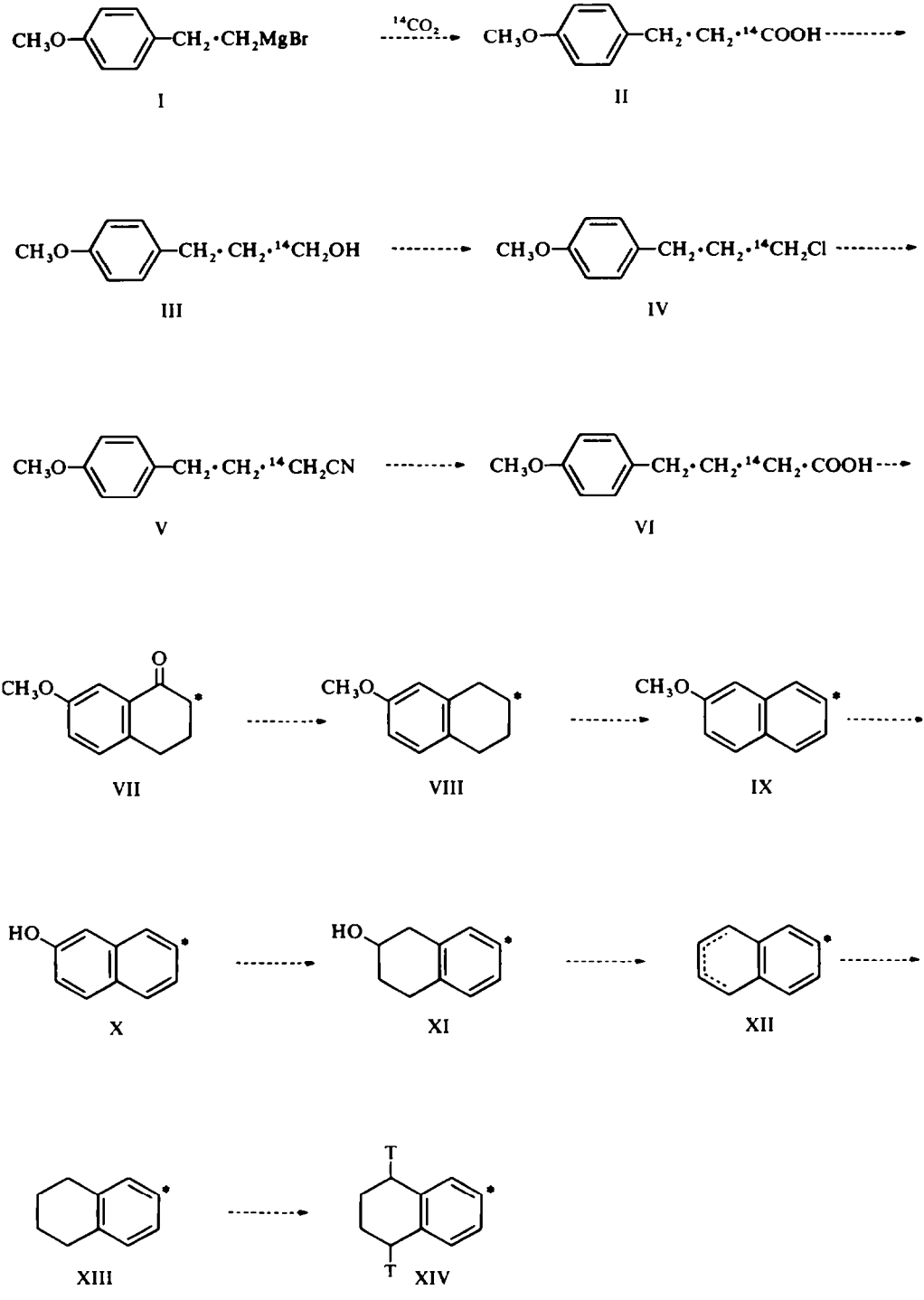
PART OF OUR INVESTIGATIONS on the chemical effects of the $\beta^-$-decay of carbon-14 is concentrated on $^{14}$C-labeled 5,6,7,8-tetrahydronaphthalene ($^{14}$C-tetralin) and $^{14}$C-labeled decahydronaphthalene ($^{14}$C-decalin).[1] We are interested in the so-called "retention factor", which can be defined as that part of the total amount of disintegrations $^{14}C \xrightarrow{\beta^-} {}^{14}N$, that results in the formation of the aza-analog of the original molecule. In order to determine the retention, after a certain decay period a quantitative determination of the formed aza-analog is necessary. Because of the long half-life of $^{14}$C the aza-analogs are formed in extremely small amounts and for that reason reversed isotope dilution has to be used to obtain reliable results.[2] This means, however, that doubly labeled molecules are required for our experiments as the $^{14}$C-label is absent in the aza-analog.[2-4] For several reasons we chose tritium as the second label. To be sure that the tritium activity of the aza-analog should be representative for the retention, we required that the tritium label has to be present in fixed, well-known positions in the molecule. This will enable us to locate the tritium label in the aza-analog in order to compare the position-bound specific activity with the total specific activity.

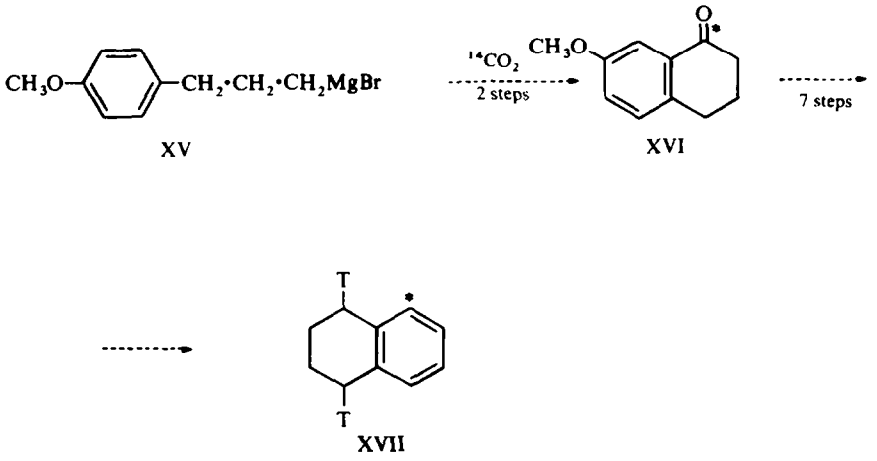
In this paper the synthesis of some doubly labeled tetralins and decalins is described. Although for our final purpose high specific activities are required, the experiments described now were carried out on a tracer level in order to establish unequivocally the position of the labels. The following compounds were prepared: (2-$^{14}$C),(5,8-$^3$H)tetralin (XIV), (1-$^{14}$C),(5,8-$^3$H)tetralin (XVII), (2-$^{14}$C),(7-$^3$H)decalin (XXI) and (1-$^{14}$C),(7-$^3$H)decalin (XXIII). In Scheme 1 and 2 the synthetic routes to these compounds are indicated.

Although most of the reactions used are well-known steps, we encountered the problem of modifying these reactions so they could be used for less than millimole

* For reasons of simplicity in the nomenclature of the labeled tetralins, we chose the less common convention of naming tetralin 5,6,7,8-tetrahydronaphthalene throughout this paper.

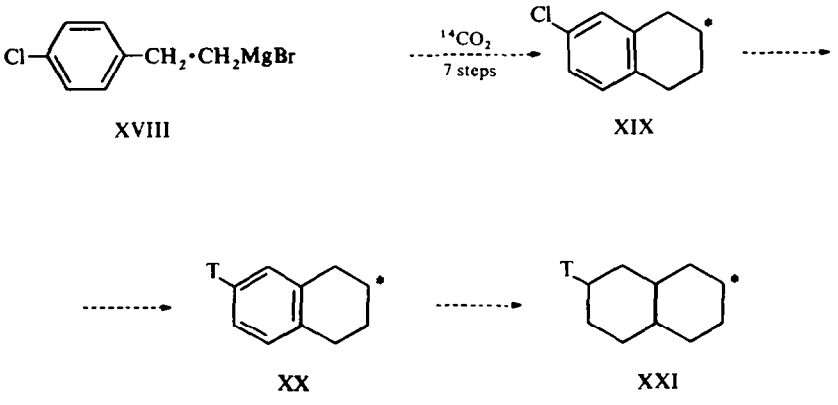
SCHEME 1
Preparation of compounds XIV and XVII



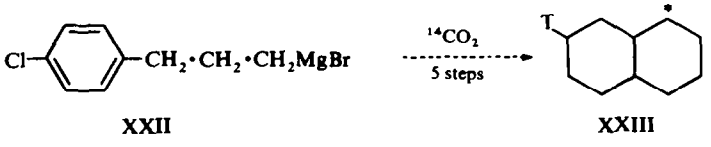



SCHEME 2

Preparation of compounds XXI and XXIII



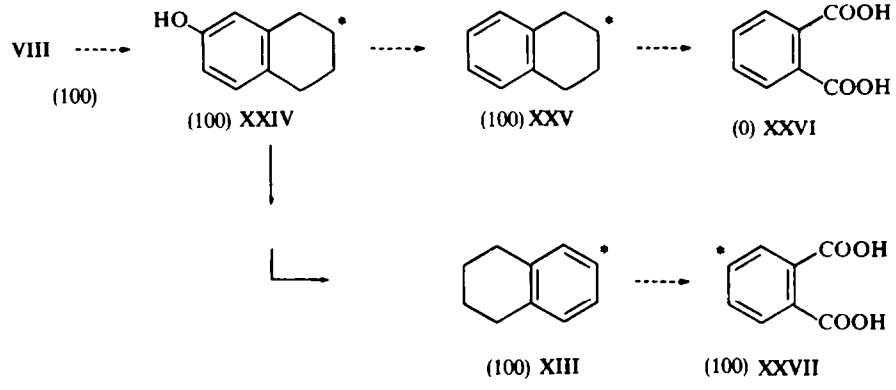

and:



amounts of highly radioactive compounds. This particulaly means prevention of contamination, thus reducing as much as possible, handling of dry material and intermediate purifications. We achieved this by carrying out most of the reactions in one sequence in a specialy designed multi-purpose extraction device.[5] In the reaction series leading to the $^{14}$C-labeled tetralins (XIV and XVII) the first compounds which had to be purified by gas chromatography (GLC) were XIII and its 1-$^{14}$C-analog, in the reaction series leading to the $^{14}$C-labeled decalins (XXI and XXIII), compound XIX and its 8-$^{14}$C-analog were the first ones to be purified.

As can be seen in Scheme 1, tetralin labeled with $^{14}$C in the aliphatic ring (VIII) was converted into tetralin labeled with $^{14}$C in the aromatic ring (XIII). We checked this conversion with the 7-$^{14}$C-compound (VIII) in the following way (Scheme 3). Part of compound VIII was isolated and purified by GLC. After determination of its specific activity the methyl ether was cleaved and the 2-hydroxytetralin obtained was converted into its phenyltetrazolyl ether. Catalytic hydrogenolysis of this ether produced (6-$^{14}$C)tetralin.[6] After purification by GLC and determination of its specific activity, the (6-$^{14}$C)tetralin was degraded to phthalic acid by permanganate oxidation.[7] The phthalic acid was isolated and purified by GLC as its dimethyl ester. Activity measurements showed that this ester was nearly inactive, thus proving that none of the $^{14}$C was located at the 5- or 8-positions of VIII.

SCHEME 3. Degradation of compound VIII and XIII

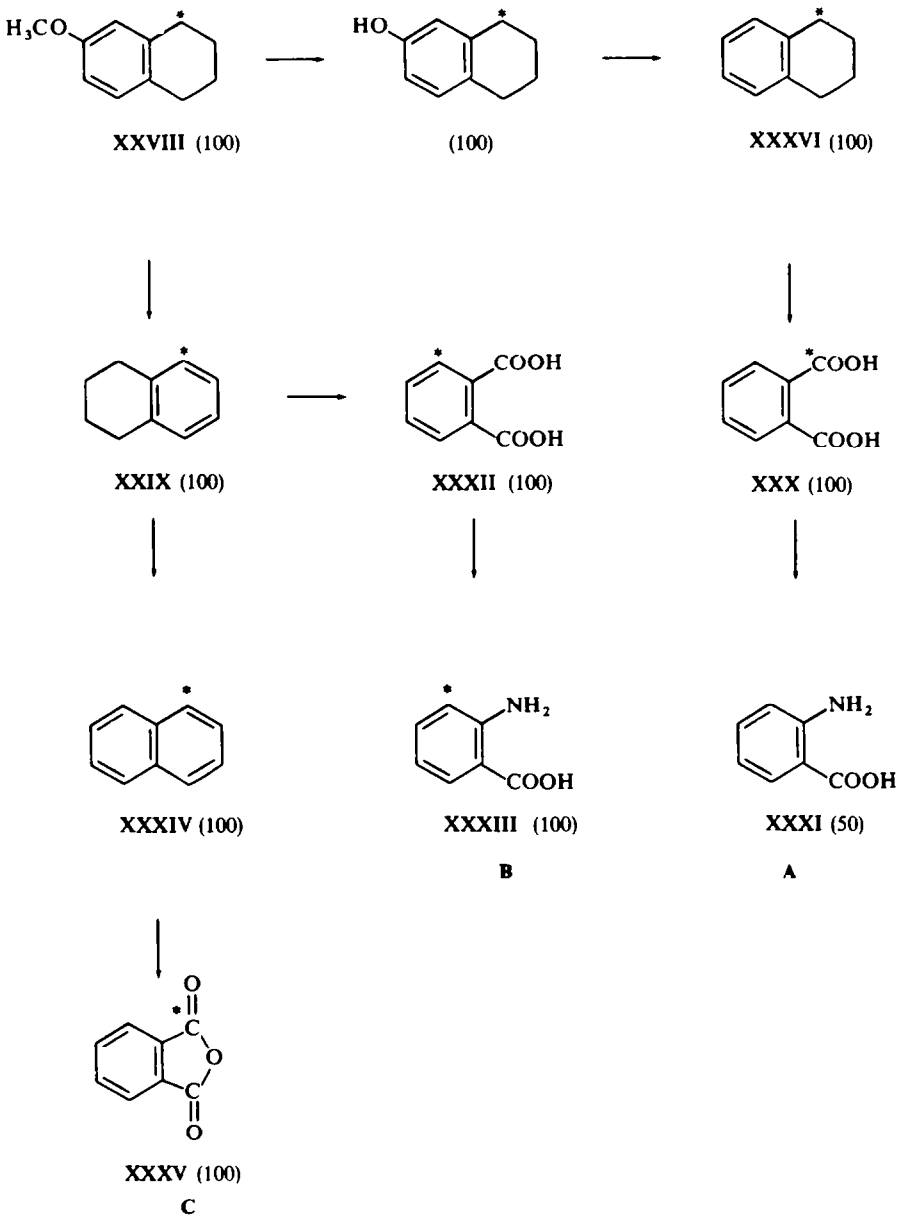



The values between brackets represent relative specific activities.

Another sample of compound VIII was converted into XIII as indicated in Scheme 1. After isolation and purification by GLC, its specific activity was the same as compound VIII. Part of compound XIII was then oxidized to phthalic acid. The observation that its specific activity was equal to those of XIII and VIII proved the location of the $^{14}$C in the newly formed aromatic ring.

Application of Scheme 3 to the 8-$^{14}$C-labeled tetralin derivative (XXVIII) is not very useful in providing information on the position of the $^{14}$C-label. Therefore, Scheme 3 was extended as represented in Scheme 4:

SCHEME 4. Degradation of XXVIII and XXIX




The values between brackets represent relative specific activities

Compound XXVIII was converted into phthalic acid (XXX) as described for VIII, but the location of $^{14}$C in a carboxylic group was proved by a Schmidt-degradation to anthranilic acid (XXXI). After conversion of XXVIII into XXIX as indicated in

Scheme 1, the location of $^{14}C$ in the newly formed aromatic ring was proved by oxidation to phthalic acid (XXXII) followed by a Schmidt-degradation to XXXIII. The 1-position of $^{14}C$ in the newly formed aromatic ring was proved by conversion of XXIX to naphthalene (XXXIV), followed by a catalytic oxidation to phthalic anhydride (XXXV).

The conclusions which can be drawn from the specific activities indicated in Scheme 4 concern the presence or absence of $^{14}C$ in the carboxylic groups of XXX and XXXII in reaction series A and B respectively, and the absence of $^{14}C$ in position 2 of XXXIV (series C).

*The introduction of the $^{3}H$-label into tetralin and decalin*

We planned to introduce the $^{3}H$-label by a direct or indirect substitution of the hydroxyl group of 7-hydroxytetralin-1(resp. 2)-$^{14}C$ (XI) and of 7-hydroxy-decalin-1(resp. 2)-$^{14}C$. The 7-hydroxytetralin-1(resp. 2)-$^{14}C$ became automatically available in our reaction sequence (Scheme 1) as to our knowledge the conversion of aliphatic to aromatic $^{14}C$-labeled tetralin can only be done if use is made of the hydrogenation characteristics of 2-hydroxynaphthalene.[8]

Meyers[9] found that 1-hydroxytetralin is an intermediate in the catalytic reduction of 1-hydroxynaphthalene to 1-hydroxydecalin. We established that 2-hydroxydecalin could be obtained from 2-hydroxytetralin under the same conditions as given by Meyers. As this 2-hydroxytetralin can easily be obtained by ether cleavage of 2-methoxytetralin (VIII), a simple way for the preparation of 7-hydroxydecalin-1-(resp. 2)-$^{14}C$ was available.

In experiments to substitute the thus obtained aliphatic hydroxyl group in tetralin and decalin for tritium, we encountered serious problems. Two principles guided us in chosing a suitable method, the yield had to be high as the overall yield of the $^{14}C$-labeled parent compounds was already low and a high specific tritium activity must be attainable.

We tried two methods, *e.g.* the reduction of the tosylate and the conversion of the hydroxyl group into a halogen followed by catalytic dehalogenation. We found that the tosylates could be obtained in good yields.[9] However, the reduction with $NaBH_4$ or LAH gave low yields. Besides the formation of an appreciable amount of elimination products, large quantities of tritium gas escape during the reaction and tritiated LAH is not commercially available, so we decided to discard the tosylate method.

The conversion of the aliphatic alcohol group of tetralin into a halogen was not very efficient, the highest yield obtained was only 55%.[10] The conversion of hydroxy-decalin into halogenated decalin was possible in yields exceeding 90%.[11] However, catalytic dehalogenation of the chloro- and bromo-compounds was impossible under our conditions and if iodo-compounds were used mainly elimination occurred. Therefore, the dehalogenation method had to be abandoned.

We did not try the decomposition of a Grignard-compound with tritiated water, as water of high specific activity had to be synthesized and because the large isotope effect in the decomposition of a Grignard compound acts in the unwanted direction.[12]

We decided therefore to abandon our first plan to introduce selectively a $^{3}H$-atom into one well-known position of the tetralin molecule and based the tritium labeling on the catalytic H–T-exchange of the α-positions with molecular tritium.[6] Compound XIII and its 1-$^{14}C$-analog were tritiated in this way (Scheme 1).

As the introduction of a $^3$H-label into decalin *via* the tosylate by reduction with tritiated $NaBH_4$ or LAH or *via* the bromide by catalytic dehalogenation with tritium gas failed to give tritiated decalin in satisfactory chemical and radiochemical yields, and as labeling by a catalytic H–T-exchange is impossible, we had to look for a method to introduce the $^3$H-label at an earlier stage in the sequence. Weitkamp[13] demonstrated that naphthalene can be hydrogenated to tetralin and tetralin to decalin. The hydrogenation of tetralin with molecular hydrogen at 50 atm in cyclohexane and Rh/C as catalyst proved to be very useful in our case. We found in separate experiments that (2-$^2$H)tetralin was converted into $^2$H-decalin without any change in the mode of deuterium labeling as indicated by the mass spectra. Furthermore, the reduction of (2-$^3$H)tetralin of known specific activity produced $^3$H-decalin of the same specific activity. We suppose therefore that the similarity of the mass spectra and the constancy of the specific activity are strong indications for the absence of hydrogen migration within the molecule during the hydrogenation and that the hydrogen label is present at the 2-position of decalin. We prepared (2-$^{14}$C), (7-$^3$H)-decalin (XXI) from (7-$^{14}$C), (2-$^3$H)tetralin (XX), the latter being obtained by catalytic dehalogenation of 2-chloro-(7-$^{14}$C)tetralin (XIX) with tritium gas, as described by den Hollander.[7] XIX was synthesized in the same way as VIII. Compound XXIII was produced along the same reaction path (Scheme 2).

## EXPERIMENTAL

2-*Methoxy*-(7-$^{14}$C)*tetralone*-8 (VII). The six steps involved in this synthesis, starting with $^{14}CO_2$ and the Grignard of 1-bromo-2-(*p*-methoxyphenyl)ethane (I), were similar to the steps described for the synthesis of 2-chloro-(7-$^{14}$C)tetralone-8.[1] The ring closure of VI was carried out as described by House and McCaully.[14] The overall yield of VII was 63% based on the amount of $^{14}CO_2$ consumed.

2-*Methoxy*-(7-$^{14}$C)*tetralin* (VIII). The catalytic reduction of VII was carried out similarly to the procedure described by Hartung and Crossley.[15] After distilling the solvent from VII, 30 ml of abs. EtOH and 100 mg of Pd/C (10%) were added. The reaction vessel was then equipped with a gas inlet[5] and hydrogen gas introduced until uptake ceased. The reduction was started by gentle heating and stirring of the vessel. After the reduction of water (70 ml) were added and VIII isolated by continuous extraction with petroleum ether b.p. 28–40°. Yield 0·79 mmol = 59% based on 1·34 mmol of starting $^{14}CO_2$.

2-*Methoxy*-(7-$^{14}$C)*naphthalene* (IX). This compound was prepared analogously to the procedure described by Braude *et al.*[16] From a solution of 0·79 mmol of VIII in petroleum ether the solvent was distilled off and replaced by benzene. After azeotropically drying by distillation under reduced pressure to a volume of 10 ml, 5 equivalents of 2,3-dichloro-5,6-dicyano-quinone (DDQ) were added under $N_2$ and the mixture refluxed for 16 hr. Then water (20 ml) and KOH (200 mg) were added and the mixture refluxed for another hr. All remaining solids were dissolved by adding tetrahydrofuran (5 ml). Compound IX was then isolated by continuous extraction with ether. After replacement of solvent by petroleum ether b.p. 28–40°, IX was roughly purified by chromatography on alumina. Yield 0·55 mmol (70%).

2-*Hydroxy*-(7-$^{14}$C)*naphthalene* (X). Methoxy ether IX was cleaved according to the procedure of McOmie.[17] Compound IX was first freed from solvent by distillation and then azeotropically dried by distillation with benzene under reduced pressure. After removal of benzene dichloromethane (20 ml) was added and a drying tube connected to the outlet of the condensor. The vessel was cooled to − 40° and immediately $BBr_3$ (3 mmol) in dichloromethane (3 ml) were added. The mixture was stirred for 2 hr at −40° and for 1 hr at room temperature, followed by refluxing for about 2 min. After carefully decomposing excess $BBr_3$ with water, X was isolated by continuous extraction with ether. Yield 0·51 mmol (92%).

7-*Hydroxy*-(2-$^{14}$C)*tetralin* (XI). This compound was prepared as described by Adkins.[18] From a solution of 0·51 mmol of X in ether the solvent was distilled off and replaced by abs EtOH. This solution together with 200 mg of a copper chromite catalyst (100–130 mesh)[19] was placed in a small-sized autoclave and shaken for 7 hr at 120–130° under $H_2$ pressure of 150–170 atmospheres. The chosen reaction temperature was 70–80° lower than indicated by Adkins, as otherwise the naphthol disappeared from the glass container in the autoclave. This could cause serious contamination without reaction as the catalyst naturally

remained in the glass container. After reaction some water was added and compound XI isolated by continuous extraction with ether. Yield 0·41 mmol (80%).

5,6-*Dihydro*-(2-$^{14}$C)*naphthalene* (XII). Compound XI (0·41 mmol) was freed from solvent and redissolved in benzene. This solution was dried azeotropically to 20 ml. Then a small excess of methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt[20, 21] was added and the mixture stirred for 15 min at room temperature and for 30 min at reflux temperature. The mixture was decomposed by stirring for 15 min at room temperature with 5% HCl aq (20 ml). XII was isolated by continuous extraction with ether. Yield 0·30 mmol (70%).

(2-$^{14}$C)*Tetralin* (XIII). To a solution of 0·30 mmol of XII in 25 ml of THF were added 50 mg of Pd/C (10%). Hydrogenation was carried out at 25° for 2 hr. After reduction 50 ml of water were added and XIII was isolated by continuous extraction with ether. Purification of XIII was carried out by GLC on Carbowax-20M (5% w/w + 5% w/w KOH on Chromosorb-W). Yield 0·28 mmol (95%).

(2-$^{14}$C), (5,8-$^{3}$H)*Tetralin* (XIV). Compound XIII was selectively labeled with tritium on the 5- and 8-position by catalytic hydrogen-tritium exchange on $Pd/CaCO_3$ as described elsewhere.[6] After purification by GLC on Carbowax-20M (5% w/w + 5% w/w KOH on Chromosorb-W), 0·26 mmol of XIV was obtained (90%).

2-*Methoxy*-(8-$^{14}$C)*tetralone*-8 (XVI). This compound was synthesized in the same way as VII, but this time from 4-(*p*-methoxyphenyl)-(1-$^{14}$C)butyric acid. The butyric acid was obtained by reaction of $^{14}CO_2$ with the Grignard of 1-bromo-3-(*p*-methoxyphenyl)propane (XV) as described by den Hollander.[1] Overall yield of XVI from $^{14}CO_2$ was 86%.

(1-$^{14}$C), (5,8-$^{3}$H)*Tetralin* (XVII). Synthetic route and purification were the same as for compound XIV. Overall yield from XVI was 30%.

(2-$^{3}$H), (7-$^{14}$C)*Tetralin* (XX). This compound was prepared as described by den Hollander.[1, 7] Purification was done by GLC on Carbowax-20M (vide supra). Overall yield was 39%.

(2-$^{14}$C), (7-$^{3}$H)*Decalin* (XXI). Compound XX was dissolved in 5 ml of cyclohexane and 50 mg of Rh/C-catalyst (10%) were added.[13] Hydrogenation was carried out in a small-sized autoclave under $H_2$ pressure of 50 atmospheres by shaking for 5 hr at room temperature. Compound XXI was isolated by continuous extraction with ether. Purification was carried out by CLG on Carbowax-20M (vide supra). Yield 90%.

(1-$^{14}$C), (7-$^{3}$H)*Decalin* (XXIII). Synthetic route and purification were the same as for XXI, but this time starting from 1-bromo-3(*p*-chlorophenyl)propane (XXII). Overall yield from $^{14}CO_2$ was 46%.

*Activity measurements and labeling specificity*

All compounds, except $^{14}CO_2$, were purified by GLC as described and were subsequently dissolved in benzene. The specific activity of the compounds was determined by gaschromatographic concentration determination *via* comparison with a series of standard solutions and activity determination of the solution by liquid scintillation counting.* The mean error on specific activities thus determined amounts to an average of 2%.

*Location of the* $^{14}$C-*label in* VIII *and* XIII (Scheme 3). In order to ascertain the position of the $^{14}$C-label in compound VIII and XIII, the following compounds were prepared and their specific activities determined.

2-*Hydroxy*-(7-$^{14}$C)*tetralin* (XXIV). Methoxy ether VIII was purified by GLC on SE-30 (15% w/w on Chromosorb-W), its specific activity was 0·425 μC/mmol. After cleavage of the ether as described for compound IX, XXIV was obtained in 90% yield.

(6-$^{14}$C)*Tetralin* (XXV). Compound XXIV was converted into its phenyltetrazolyl ether, which gave (6-$^{14}$C)tetralin by catalytic hydrogenolysis on $Pd/CaCO_3$, as described elsewhere.[6] After purification by GLC on Carbowax-20M (vide supra) its specific activity was 0·426 μC/mmol.

*Phthalic acid* (XXVI). Oxidation of XXV to phthalic acid was carried out as described by den Hollander.[7] The specific activity of its dimethyl ester was less than 0·005 μC/mmol, after purification by GLC. This result indicates that the specificity of the $^{14}$C-label in VIII was better than 99%.

(2-$^{14}$C)*Tetralin* (XIII). This compound was prepared as described before. Its specific activity was 0·428 μC/mmol, thus equal to that of VIII.

*Phthalic acid* (XXVII). Oxidation of XIII with permanganate was carried out as described before. The specific activity of its dimethyl ester was 0·427 μC/mmol, thus indicating that the $^{14}$C-label was present in the aromatic ring to at least 99·5%.

* Nuclear Chicago, Unilux I Model 6850.

TABLE 1. DEGRADATION OF COMPOUND VIII AND XIII

| Compound | Specific act. (μC/mmol) | Conclusions on the $^{14}$C-positions |
|---|---|---|
| VIII | 0·425 | |
| XXV | 0·426 | location in 7 position of VIII is > 99% |
| XXVI | <0·005 | |
| XIII | 0·428 | |
| XXVII | 0·427 | location in aromatic ring of XIII is > 99·5% |

The experimental results and conclusions are summarized in Table 1.

*Location of the* $^{14}$C-*label in* XXVIII *and* XXIX (Scheme 4). The preparation of compounds XXIX, XXX and XXXII was respectively identical to that of XIII, XXVI and XXVII. Compound XXXIV was prepared as indicated for IX. The conversion of XXXIV into XXXV was carried out as described by van der Jagt *et al.*[22] The Schmidt-degradation of XXX and XXXII was carried out as described by Leete.[23] The resulting anthranilic acid was isolated by continuous extraction from an acidic medium pH = 5, converted into its methyl ester by reaction with $CH_2N_2$ and purified by GLC on SE-30 (15% w/w on Chromosorb-W). The results of the above mentioned conversions and degradations are summarized in Table 2.

TABLE 2. DEGRADATION OF COMPOUND XXVIII AND XXIX

| Compound | Specific act. (μC/mmol) | Conclusions on the $^{14}$C-positions |
|---|---|---|
| XXVIII | 3·18 | location in 8-position of XXVIII is > 97% |
| XXXVI | 3·20 | |
| XXX | 3·25 | |
| XXXI | 1·69 | |
| and | | |
| XXIX | 3·28 | location in aromatic ring of XXIX is > 96% |
| XXXII | 3·21 | |
| XXXIII | 3·17 | |
| XXIX | 3·28 | location in 1-position of XXIX is > 94% |
| XXXIV | 3·23 | |
| XXXV | 3·09 | |

However, in view of the mean error of 2% on the specific activities listed in Table 2, it can be concluded that within the experimental error the $^{14}$C-position in the compounds mentioned is 100% specific.

*Location of the* $^3$H-*label in* XXI *and* XXIII. As we were unable to prepare pure (2-$^2$H)decalin by catalytic dehalogenation of 2-halodecalin, we had to introduce the hydrogen label at an earlier stage. Catalytic hydrogenation of specifically deuterated tetralin produces deuterated decalin. However, this method has the disadvantage that no absolute proof can be given on the position of the label in the produced decalin. The hydrogenation was carried out as described before, with either EtOD or cyclohexane as solvent.

*Ethanol-OD.* 0·8 mmol unlabeled tetralin was dissolved in 5 ml EtOD and 35 mg Rh/C (10%) were added. After hydrogenation at 50 atm. for 18 hr at room temperature decalin was isolated and purified by GLC. Its mass spectrum showed that 9·85 D-atom/molecule was introduced, while the species present were labeled up to $D_{17}$.

*Cyclohexane.* (2-$^2$H)tetralin was prepared as described by den Hollander.[7] Its mass spectrum showed the presence of $D_0$ = 48·1%, $D_1$ = 50·8% and $D_2$ = 1·12%. 0·5 mmol of (2-$^2$H)tetralin was converted into $^2$H-decalin as described for compound XXI. After isolation and purification by GLC, the mass spectrum of $^2$H-decalin showed the presence of $D_0$ = 48·6%, $D_1$ = 49·8% and $D_2$ = 1·54%. Furthermore, we found that after catalytic hydrogenation of (2-$^3$H)tetralin with a specific activity of 2·64 μC/mmol, $^3$H-decalin was obtained which specific activity was the same as that of (2-$^3$H)tetralin within the experimental error.

We inferred from these results that no hydrogen scrambling took place during the hydrogenation and that the hydrogen label in decalin was still present at the same position as in the original tetralin.

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