Tetrahedron Letters No.59, pp. 6245-6248, 1968. Pergamon Press. Printed in Great Britain.

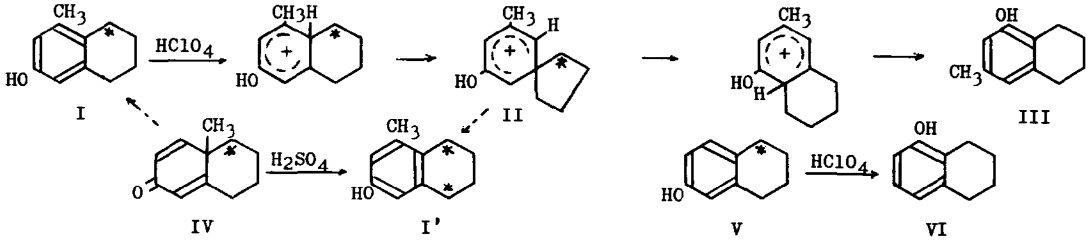
TRACER STUDIES ON THE MECHANISM OF THE PHENOL-PHENOL REARRANGEMENT

Reiji Futaki

Hoshi College of Pharmacy, 2-Ebara, Shinagawa-ku, Tokyo, Japan

(Received in Japan 21 October 1968; received in UK for publication 14 November 1968)

Dreiding's [1] finding of the phenol-phenol rearrangement of 1-methyl-3-tetralol (I) to 3-methyl-1-tetralol (III) on treatment with 70% perchloric acid and the proposed mechanism involving spiro-intermediate (II) suggested to the author the examination of another possible mechanism which also could explain the location of ^{14}C at position 6 and 9 in 1-methyl-3-tetralol (I') obtained by the dienone-phenol rearrangement of 10-methyl-1,4-hexadien-3-one$[9-^{14}C]$(IV) on treatment with aqueous 50% sulphuric acid, as stated in the previous paper.[2] It can be supposed that a simple 1,2-shift of the angular methyl group to give (I)$[9-^{14}C]$ and subsequent automerisation via a spirointermediate, (I'←-- II), may give rise to (I'), the labelled position isomer.



Here the author wishes to report this possibility must be ruled out because in the present investigation no automerisation was found in the treatment of independently synthesised (I)$[9-^{14}C]$ with the specified dienone-phenol rearrangement conditions.

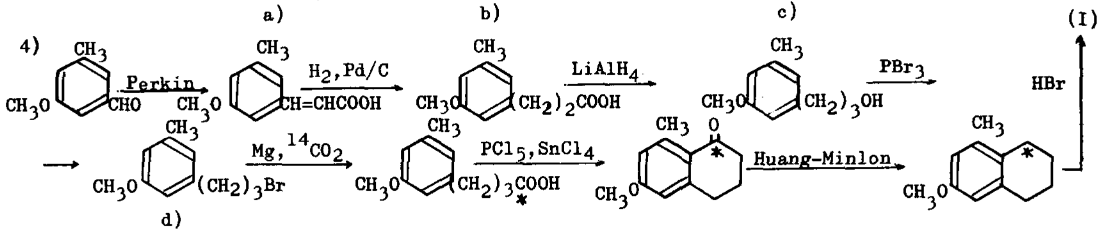
Further the proposed mechanism was studied to see if it could account for the location of ^{14}C in (III) obtained by the phenol-phenol rearrangement of (I)$[9-^{14}C]$ on treatment with 70% perchloric acid. The data show that position 6 in both (III) and recovered (I) carry only very small amounts of ^{14}C, 0.3% and 1.2% respectively, and it turns that nearly all the ^{14}C is located at positions 9. This means that the rearrangement passed through a mainly 1,3-shift of 9-10 linkage to position 4, with only a slight concurrent spirointermediate shift.

A similar study was made of the phenol-phenol rearrangement of 3-tetralol[9-^{14}C](V) to 1-tetralol (VI). The results show the same tendency as before except more movement by the spiro-intermediate pathway, resulting in 6% of ^{14}C at position 6 in (VI), and a fall in recovered (V) at position 9 (-17%).

Preparation of the labelled compounds:

3-Tetralol[9-^{14}C](V) was prepared in the previous work.3)

1-Methyl-3-tetralol[9-^{14}C](I) was prepared as follows.



The Perkin reaction was carried out in usual manner, and gave 1.5g of a) starting from 3.3g of the aldehyde. The following four compounds previously unknown, all gave satisfactory results on elementary analysis.

a) needles(from benzine), mp 129°, (on Kofler block, uncorr.)
b) prisms, mp 17-18°, bp 125-130°/5mm
c) colourless liquid, bp 133-135°/5mm, $n_D^{20^\circ}$ 1.5268
d) colourless liquid, bp 125-128°/5mm, $n_D^{20^\circ}$ 1.5447

Degradation and radioactivity measurement of these labelled tetralols was carried out to confirm the labelled position before the treatment of phenol-phenol rearrangement. The results show at the same time that the foregoing preparation procedure of demethylation with boiling HBr-HOAc caused no automerisation.

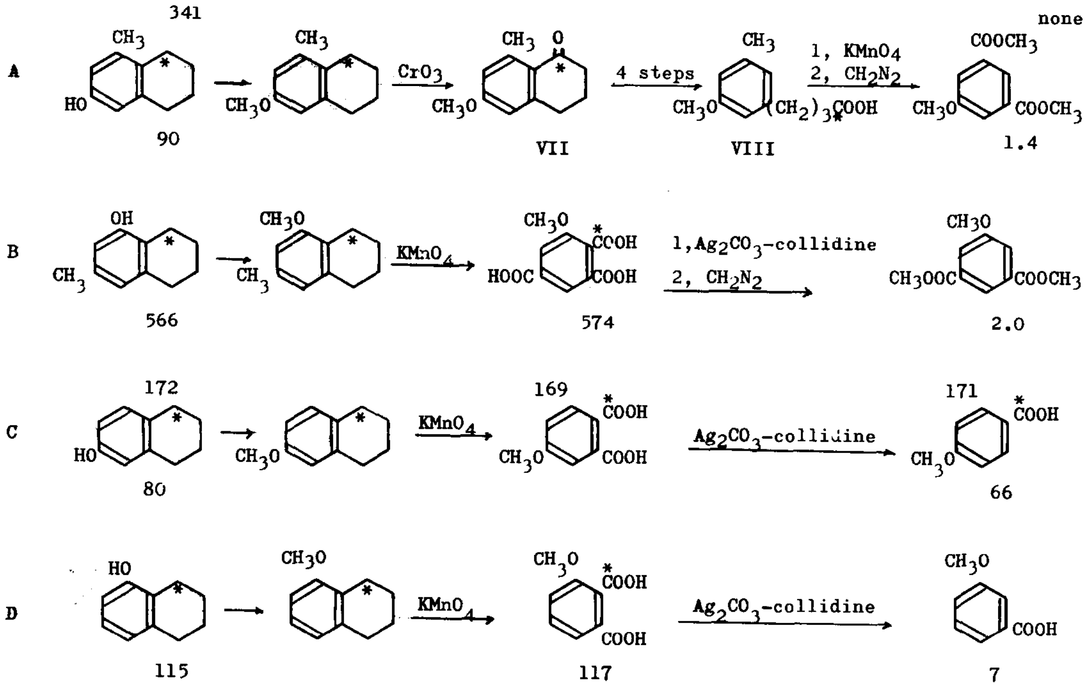
The treatment of (I)[9-^{14}C] with aqueous 50% sulphuric acid at 100° for 30 min, the specified dienone-phenol conditions5), was also found to cause no automerisation.

Rearrangement

0.5 g of each (I)[9-^{14}C] and (V)[9-^{14}C] was stirred with 10 ml of 70% perchloric acid at 80° for 2 hr. Each dark reaction mixture was extracted with ether, distilled in vacuo, and chromatographed (Al_2O_3-CCl_4) to get good separation. The yield of sum total was 84% in the former and 39% in the latter. The ratio of 3-ol : 1-ol was close to Dreiding's results, 1:4 and 1:1 respectively. Each pair showed the same specific radioactivity.

Degradation

After being diluted with the proper amount of carrier, each tetralol was degraded as follows, with no subsequent dilution.



In all cases satisfactory over-all yields of methylation, 85-90%, were obtained by the indirect method of treating the acetates in methanol with dimethyl sulphate and 50% KOH . Scheme A is described in the previous paper.[2] Trial radioactivity measurement of carboxylic carbon in (VIII) by the Schmidt procedure failed because of facile ring closure of the substance to give (VII). In scheme B,C and D, permanganate oxidation was carried out in the same way as previously described[3], except that in scheme B boiling water-bath temperature was necessary in the first alkaline oxidation. Decarboxylation was also carried out in the same way as in the previous paper[3], except for gentle boiling of the reaction mixture for 1 hr, and gave only the desired acids as above.

Identification of these carboxylic acids was carried out by mixed melting point determination with the authentic specimens and their methyl esters.

Radioactivity measurement

Around 4.500mg of the samples were mounted on stainless-steel dishes(ϕ2.5cm) prevented from creeping to maintain a thickness of 0.9mg/cm^2, and counted by a 2π-gasflow counter (background 3.4) . Counts per minute ranging from a few hundred to over a thousand were usual, and net cpm not less than background was treated as significant.

Numbers at the top of each formula mean cpm/10^{-2}m mol before the rearrangement treatment, and those at the bottom mean after it. Astrisks show main location of ^{14}C.

The author wishes to express his thanks to Miss. M.Kawamura and Mr. T.Hirabayashi for their technical assistance , and also to Miss. T.Yamaya for elementary analysis.

References

1) W.H.Hopff and A.S.Dreiding, Angew. Chem. 77, 717 (1965)

2) R.Futaki, Tetrahedron Letters, No.26 2455 (1967)

3) R.Futaki, ibid., No, 41, 3059 (1964)

4) T.Tsuda,S.Ikuma,M.Kawamura,R.Tachikawa, Y.Baba and T.Miyadera, Chem.Pharm.Bull.Japan 10, 857, (1962)
W.F.Beech, J.Chem.Soc. 1297 (1954)

5) A.S.Dreiding, W.J.Pummer and A.J.Tomasewski, J.Am.Chem.Soc. 75,3159 (1953)