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Coal Chemistry. 8. Reactions of Tetralin with Coal and with Some Carbon-14-Containing Model Compounds[1]

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Abstract: When coal was treated with tetralin-*1*-^{14}C at 400 °C, small yields of α- and β-methylnaphthalenes-^{14}C were observed. In order to determine the mechanism of the reaction, tetralin was heated with ^{14}C-labeled 1,3-diphenylpropanes (**1**), with 1,3-diphenylpropene (**2**), and with ^{14}C-labeled phenetoles (**3**). In each case methylnaphthalenes were observed, and the origins of the methyl groups were determined with carbon-14. In addition to the methylnaphthalenes, **1** and **2** also yielded toluene and ethylbenzene (after 19 h), whereas phenetole-β-^{14}C (**3**-β-^{14}C) yielded toluene (unlabeled) plus ethyl-^{14}C-benzene, benzene, phenol, and a mixture of α- and β-ethyl-^{14}C-naphthalenes. Crossover experiments with labeled phenetole and unlabeled ethyl *p*-tolyl ether proved the intramolecularity of the reaction phenetole → toluene + ethylbenzene, thus illustrating a 1,2-phenyl shift from oxygen to carbon.

Introduction

Tetralin was the original "hydrogen donor" in the Pott-Broche process[2] for the solvent extraction of coal, and, although it was later replaced with recycled oils, it is still employed in coal research as the archetypal donor solvent.[3]

We have already established[4,5] that Illinois No. 6 vitrain is a better hydrogen donor, for several receptors, than tetralin. In a later study[6] several coals and a series of organic compounds were tested as hydrogen donors for the reduction, at 400 °C, of benzophenone to diphenylmethane. Tetralin did not place very high as a hydrogen donor by this criterion, and, with the exception of anthracite, did not score as well as the several other coals tested. Further, solvent-refined coal often exhibits little or no increase in hydrogen content.[3] The results just mentioned raise several obvious questions concerning the role of tetralin in coal conversion processes. In order to gain more information on the subject, we prepared tetralin-*1*-^{14}C[7] and studied its reactions with Illinois No. 6 vitrain at 400 °C for various periods of time. In the recovered solvent we found traces of carbon-14-labeled α- and β-methylnaphthalenes, representing 3% by weight of the original coal sample. Since the product contained carbon-14, the naphthalene residue came from the tetralin-*1*-^{14}C. Tetralin alone, at 400 °C for 18 h, gives no observable trace of methylnaphthalenes; we presume, therefore, that the methyl carbons had their origin in coal. In order to test this possibility, we investigated the reactions of tetralin and of tetralin-*1*-^{14}C with several labeled and unlabeled model compounds.[4,5] We report here on the reactions, with tetralin at 400 °C, of (a) 1,3-diphenylpropane (**1**) and its isotope position isomers **1**-*1*-^{14}C and **1**-*2*-^{14}C; (b) 1,3-diphenylpropene (**2**), and (c) phenetole (**3**) and **3**-α-^{14}C and **3**-β-^{14}C.

$Ph\overset{*}{C}H_2CH_2CH_2Ph$ **1**-*1*-^{14}C

$PhCH_2\overset{*}{C}H_2CH_2Ph$ **1**-*2*-^{14}C

$PhCH{=}CHCH_2PH$ **2**

$PhO\overset{*}{C}H_2CH_3$ **3**-α-^{14}C

$PhOCH_2\overset{*}{C}H_3$ **3**-β-^{14}C

Methods and Results

The starting materials were prepared by standard methods (see Experimental Section). On prolonged heating (19 h) with tetralin, **1**, **2**, and **3** all undergo considerable reaction. Tetralin itself, under these conditions yields, in addition to naphthalene, small amounts of indan and methylindan, plus traces of other materials.[8] Given in Table I are the yields, expressed in mole percent, of the major products derived from **1**, **2**, and **3** (compounds derived from tetralin alone[8] are omitted). As is apparent from Table I, 1,3-diphenylpropane (**1**) and 1,3-diphenylpropene (**2**) react with tetralin to produce toluene, ethylbenzene, and α- and β-methylnaphthalenes. Phenetole, in addition, yields a mixture of α- and β-ethylnaphthalenes plus benzene and phenol; that the naphthalene moieties of these products come from the tetralin and the alkyl moieties from the 1,3-diphenylpropane and phenetole can be seen from the results of the experiments with labeled reactants, presented in Figures 1 and 2. The reactions were also carried out by heating **1** and **3** (unlabeled) with tetralin-*1*-^{14}C for 18 h at 400 °C; only the alkylnaphthalenes produced during these experiments contained carbon-14. Each product was isolated by preparative GC and identified by its NMR spectrum. The radioactivity distributions shown in Figures 1 and 2 were determined by GC combined with a carbon-14 monitor;[9] by comparing areas under the appropriate peaks, it could be determined that the toluene and ethylbenzene obtained from **1**-*1*-^{14}C contained half (±4%) the molar radioactivity of the reactant. Similar comparisons for the products of reaction of the two isotope position isomers of **3** were attempted, but consistent results could not be obtained. Consequently, the toluene and ethylbenzene fractions produced from **3**-β-^{14}C and **3**-α-^{14}C were isolated and their molar radioactivities or those of the benzoic acid samples obtained on oxidation were determined.[10] The results are shown in Figures 3 and 4, and require some comment. The errors in molar radioactivities of Figures 3 and 4 are beyond normal limits because of difficulties in combusting volatile liquids. The data show, nonetheless, that

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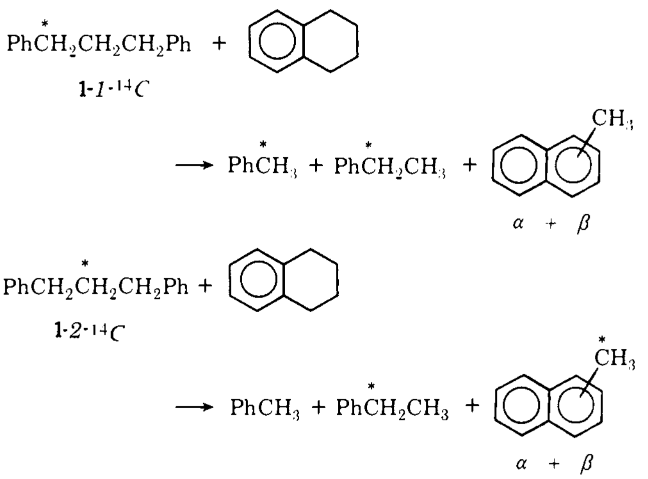


Figure 1. ^{14}C tracer results for the reactions of 1,3-diphenylpropane-*1*-^{14}C and -*2*-^{14}C with tetralin at 400 °C, 18 h.

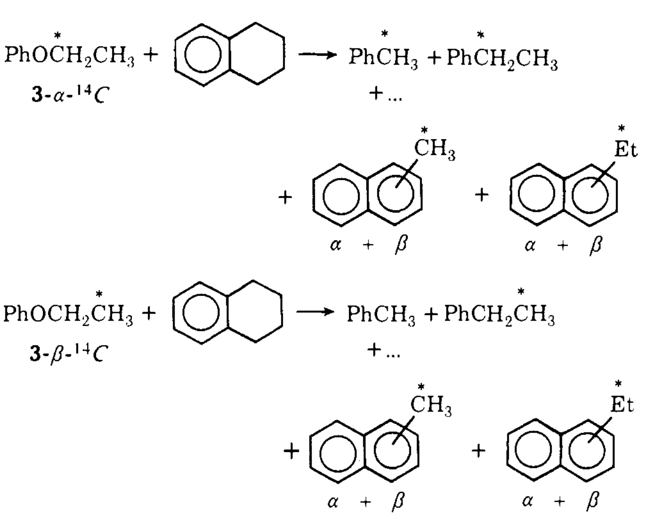


Figure 2. ^{14}C tracer results for the reactions of phenetole-α-^{14}C and phenetole-β-^{14}C with tetralin at 400 °C, 18 h.

Table I. Yields, in Mole Fractions, of Major Products from the Reactions of Tetralin with 1,3-Diphenylpropane (**1**), with 1,3-Diphenylpropene (**2**) and with Phenetole (**3**) at 400 °C, 18 h

products	reactant[a] 1	2	3[b]
benzene	0	0	0.12
phenol	0	0	0.54
toluene	0.56	0.53	0.11
ethylbenzene	0.32	0.45	0.10
α,β-methylnaphthalenes	0.12	0.02	0.11
α,β-ethylnaphthalenes	0	0	0.03

[a] The yields are normalized to the sums of the products. In the case of reactants **1** and **2** there were no other identifiable products other than those arising from tetralin.[8] [b] The yields from **3** were variable.

$$Ph O C H_2\overset{*}{C}H_3 \rightarrow Ph\overset{*}{C}H_3 + Ph\overset{*}{C}H_2\overset{*}{C}H_3$$

1.78 mCi/mol 0.038 1.86

$$Ph\overset{*}{C}H_2CH_3 \rightarrow Ph\overset{*}{C}OOH$$

1.86 0.1145

Figure 3. Results of carbon-14 assays of phenetole-β-^{14}C, the toluene and ethylbenzene therefrom, and of benzoic acid produced on oxidation of ethylbenzene.

$$PhO\overset{*}{C}H_2CH_3 \rightarrow Ph\overset{*}{C}H_3 + Ph\overset{*}{C}H_2CH_3$$

5.00 mCi/mol 4.37 4.44

$$Ph\overset{*}{C}H_3 \rightarrow Ph\overset{*}{C}OOH$$

4.37 4.11

$$Ph\overset{*}{C}H_2\overset{*}{C}H_3 \rightarrow Ph\overset{*}{C}OOH$$

4.44 4.04

Figure 4. Results of carbon-14 assays of phenetole-α-^{14}C, and the benzoic acid samples obtained on oxidation of toluene-^{14}C and ethylbenzene-^{14}C.

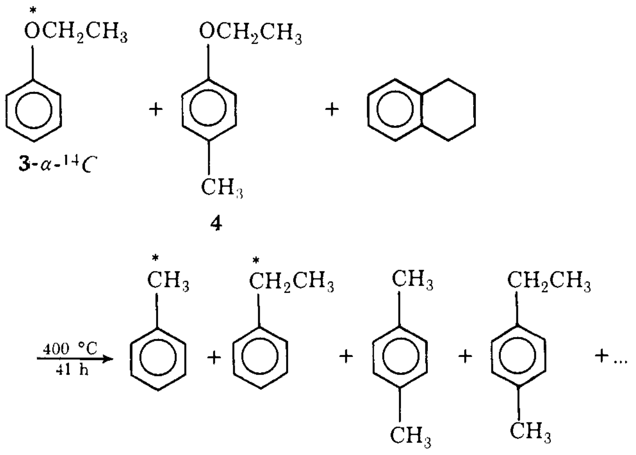


Figure 5. Results of crossover experiment between **1**-α-^{14}C and **3** showing intramolecularity of formation of toluene and ethylbenzene.

the toluene contains only 2% of the molar radioactivity of the phenetole-β-^{14}C from which it was formed. In like manner we conclude that the ethyl-^{14}C-benzene contains 6% carbon-14 in the α position and 94% in the β. The data of Figure 3 are more reliable that those of Figure 4 because of the larger errors introduced by isotope effects on oxidation of toluene-^{14}C and ethyl-*1*-^{14}C-benzene to benzoic acid.[11]

In order to determine whether the conversion of phenetole into ethylbenzene and toluene is inter- or intramolecular, a crossover experiment was carried out in which *p*-tolyl ethyl ether (**4**) was mixed with an equal portion of **3**-α-^{14}C, and the mixture was heated with tetralin for 41 h at 400 °C. The presence or absence of carbon-14 in four key products—toluene, ethylbenzene, *p*-xylene and *p*-ethyltoluene—was then determined. The results are shown in Figure 5.

When the reactions between **1** and tetralin were carried out for shorter periods of time (up to 1 h) it was possible to isolate and identify 1- and 2-β-phenethyltetralin through their NMR spectra. GC-MS analyses confirmed the identities of these structures, and gave evidence as well for traces of styrene, methyltetrahydronaphthalenes, diphenylpropene, and very minor amounts of several other compounds.

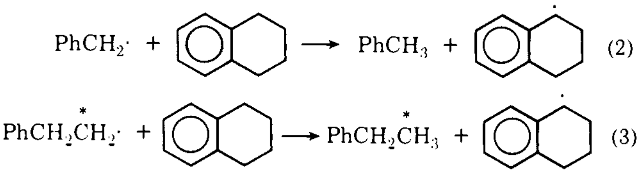
GC-MS analyses of the products of reaction of phenetole with tetralin at 400 °C revealed the presence of trace amounts of substances tentatively identified as ethyltetralins and hydroxyethylbenzene, plus the decomposition products[8] of tetralin.

Discussion

Some interesting facts are apparent from Figures 1-4 and from the other data presented in the previous section. (1) The methyl groups of the methylnaphthalenes produced during the reaction of tetralin with 1,3-diphenylpropane (**1**) come only from the no. 2 carbon of 1,3-diphenylpropane, whereas (2) the methyl groups of the methylnaphthalenes produced from phenetole (**3**) come from both the α and β positions of phenetole, and (3) although the toluene produced from phenetole-α-^{14}C is labeled, that produced from phenetole-β-^{14}C (except for a 2% residual) is not.

We will consider first the reactions of 1,3-diphenylpropane with tetralin, whose primary pathways seem to be explained best by the mechanism portrayed in reactions 1-9. The dihydronaphthalene formed in step 10, being a better hydrogen donor than tetralin,[4] is converted into naphthalene by processes analogous to its own formation from tetralin. Thus, all processes shown—given sufficient time—lead to toluene, ethylbenzene, and α- and β-methylnaphthalenes (plus the decomposition products of tetralin).[8] The small yield of methylnaphthalenes (2%, Table I) observed from the reaction of 1,3-diphenylpropene (**2**) with tetralin lends support to the mechanism, for **2** cannot undergo homolysis directly to yield the benzyl and phenethyl radicals (reaction 1), but must first be converted into 1,3-diphenylpropane. Evidently 1,3-diphenylpropene is converted into Ph$\dot{C}$HCH$_2$CH$_2$Ph which then undergoes reaction **5** faster than it can be converted into **1**. The yields of products from **1** (Table I) also confirm the mechanism. It can be easily shown from reactions 1-9 (x = moles of methylnaphthalenes formed *per mole* of **1**) that the yields, in mole fractions of toluene, ethylbenzene, and methylnaphthalenes, respectively, are $(1+x)/(2+x)$, $(1-x)/(2+x)$, and $x/(2+x)$ (see Appendix). When $x = 0.25$, the calculated mole percents are 0.56, 0.33, and 0.11, in excellent agreement with the experimental values of 0.56, 0.32, and 0.12.

$$\mathrm{PhCH_2\overset{*}{C}H_2CH_2Ph \longrightarrow PhCH_2\cdot + \cdot\overset{*}{C}H_2Ph} \quad (1)$$

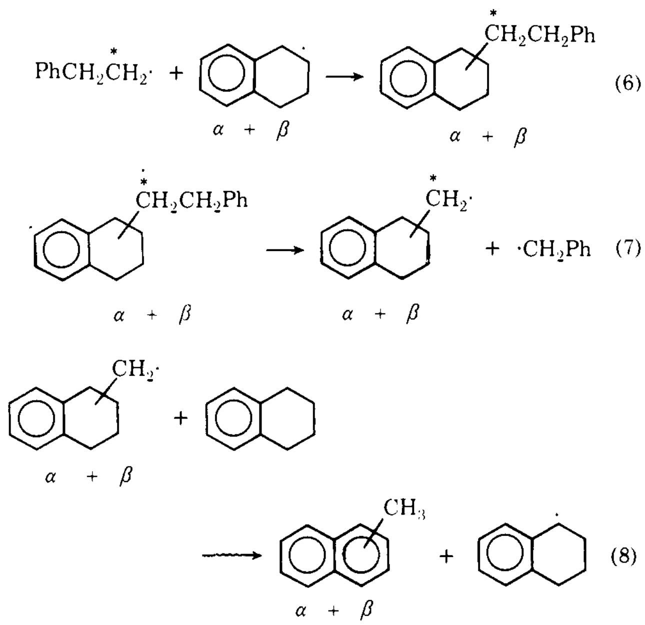


(2)

(3)

$$\mathrm{Ph CH_2\overset{*}{C}H_2\cdot + PhCH_2\overset{*}{C}H_2CH_2Ph \longrightarrow PhCH_2\overset{*}{C}H_3 + Ph\dot{C}H\overset{*}{C}H_2CH_2Ph} \quad (4)$$

$$\mathrm{Ph\dot{C}H\overset{*}{C}H_2CH_2Ph \longrightarrow PhCH{=}\overset{*}{C}H_2 + PhCH_2\cdot} \quad (5)$$

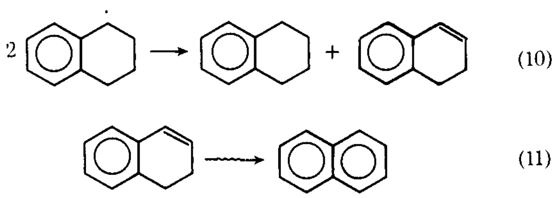


(6)

(7)

(8)

$$\mathrm{PhCH{=}\overset{*}{C}H_2 \longrightarrow PhCH_2\overset{*}{C}H_3} \quad (9)$$



(10)

(11)

We turn now to the reactions of **3** and of its isotope position isomers with tetralin. There are five conceivable pathways (reactions 12-14, 16, 17) for the homolysis of phenetole (**3**). Reaction 12 is energetically unfavorable, relative to reactions 13-17;

$$\underset{3\text{-}\beta\text{-}^{14}C}{\mathrm{PhOCH_2\overset{*}{C}H_3}} \rightarrow \mathrm{Ph\cdot + \cdot OCH_2\overset{*}{C}H_3} \quad (12)$$

$$\underset{3\text{-}\beta\text{-}^{14}C}{\mathrm{PhOCH_2\overset{*}{C}H_3}} \rightarrow \mathrm{PhO\cdot + \cdot CH_2\overset{*}{C}H_3} \quad (13)$$

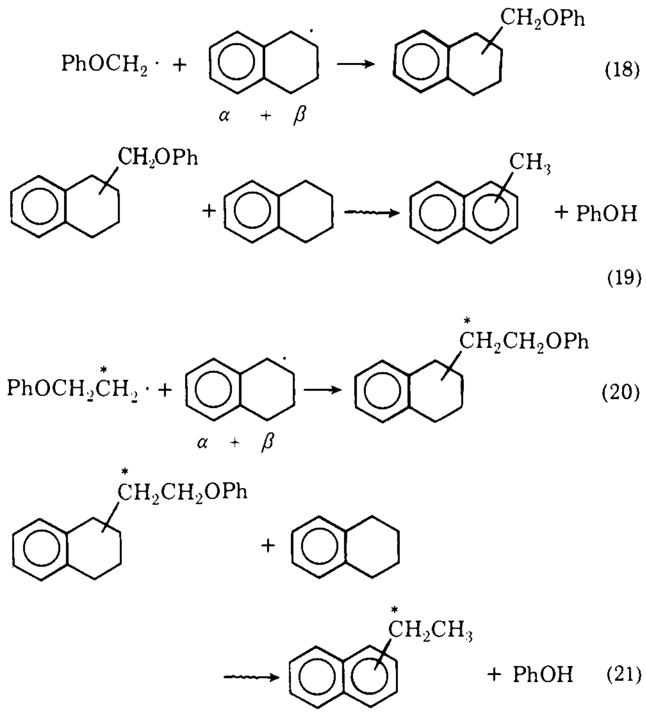
$$\underset{3\text{-}\beta\text{-}^{14}C}{\mathrm{PhOCH_2\overset{*}{C}H_3}} \rightarrow \mathrm{PhOCH_2\cdot + \overset{*}{C}H_3\cdot} \quad (14)$$

$$\mathrm{PhOCH_2\cdot \rightarrow Ph\cdot + CH_2O} \quad (15)$$

$$\underset{3\text{-}\beta\text{-}^{14}C}{\mathrm{PhOCH_2\overset{*}{C}H_3}} \mathrm{+ R\cdot \rightarrow PhO\dot{C}HCH_3 + RH} \quad (16)$$

$$\underset{3\text{-}\beta\text{-}^{14}C}{\mathrm{PhOCH_2\overset{*}{C}H_3}} \mathrm{+ R\cdot \rightarrow PhOCH_2\overset{*}{C}H_2\cdot + RH} \quad (17)$$

so the phenyl radical probably arises through an alternate path such as 15. Benzene and phenol must be produced, in part, through reactions of the phenyl and phenoxyl radicals (formed as in reactions 15 and 13) with tetralin. The methyl- and ethylnaphthalenes could conceivably be formed in various ways—for example, through the reactions of ethyl and methyl radicals with tetralin or through reactions 18-21. Toluene and ethylbenzene (except for minor amounts; see Figures 3 and 4) are produced from **3** through intramolecular reactions. This fact was demonstrated by the results shown in Figure 5. Formation of radicals in a cage at 400 °C is highly unlikely. Even



(18)

(19)

(20)

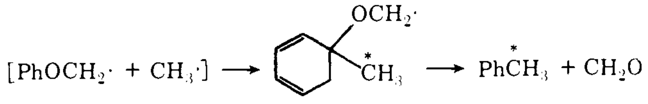
(21)

if we postulate cage formation, however, it is difficult to imagine how toluene and ethylbenzene could possibly result. Further, decomposition of the ethoxy radical formed by the very unlikely homolysis (reaction 12) of the phenyl–oxygen bond (reaction 22 followed by radical recombination (reaction

$$[\mathrm{Ph\cdot + \cdot OCH_2\overset{*}{C}H_3}] \rightarrow [\mathrm{Ph\cdot + \cdot\overset{*}{C}H_3 + CH_2O}] \quad (22)$$

$$\underset{\text{cage}}{} \qquad [\mathrm{Ph\cdot + \cdot\overset{*}{C}H_3}] \rightarrow \mathrm{Ph\overset{*}{C}H_3} \quad (23)$$

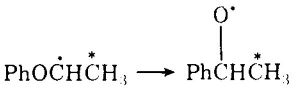
23)) would lead to the formation from phenetole-*β*-^{14}C, of labeled toluene, contrary to our observations. Ipso reactions[12,13] of the radical pairs formed (in a cage) in reactions 13 and 14 have no precedent, and in the latter case with phenetole-*β*-^{14}C as the starting material would lead (reaction 24) to labeled toluene—contrary to the facts. Consequently,



(24)

the only satisfactory explanation for the *intramolecular* production of toluene and ethylbenzene involves phenyl migration from oxygen to carbon, as in reactions 25 and 26. The radicals

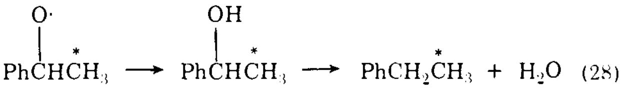
$$\mathrm{PhOCH_2\cdot \rightarrow PhCH_2O\cdot} \quad (25)$$



$$\mathrm{Ph O\dot{C}H\overset{*}{C}H_3 \longrightarrow Ph\overset{O^{\cdot}}{\overset{|}{C}}H\overset{*}{C}H_3} \quad (26)$$

so formed are then converted, in the presence of tetralin, into benzyl alcohol and *α*-phenylethanol-*β*-^{14}C, which proceed to toluene and ethylbenzene-^{14}C (eq 27 and 28). The latter re-

$$\mathrm{PhCH_2O\cdot \longrightarrow PhCH_2OH \longrightarrow PhCH_3 + H_2O} \quad (27)$$



$$\mathrm{Ph\overset{O\cdot}{\overset{|}{C}}H\overset{*}{C}H_3 \longrightarrow Ph\overset{OH}{\overset{|}{C}}H\overset{*}{C}H_3 \longrightarrow PhCH_2\overset{*}{C}H_3 + H_2O} \quad (28)$$

actions undoubtedly occur through C–O cleavage followed by hydrogen abstraction by the benzyl and 1-phenylethyl radicals.

Phenyl migration from oxygen to carbon in a free-radical reaction has been claimed,[14] but the evidence is circumstantial.

Experimental Section

All chemicals were purchased from Aldrich Chemical Co., Eastman Kodak Co., or they were prepared according to the procedures listed below. NMR analyses were performed on a Varian XL-100 spectrometer. Samples were 30% solutions in deuteriochloroform with tetramethylsilane as an internal standard. Preparative GC was performed using a Varian Aerograph Series 2800 instrument.

1,3-Diphenylpropane (1). Chalcone (25 g) was reduced in absolute ethanol (100 mL) with Raney nickel W-2 catalyst[15] at ~2-bar hydrogen pressure. The catalyst was removed by filtration, and the product was distilled (bp 125 °C (1 mm)). Yields were 55–60% (the remainder of the product was the carbinol); the purity by GC analysis was better than 95%. The NMR spectrum was consistent with the structure.[16]

1,3-Diphenylpropane-*1*-^{14}C (1-*1*-^{14}C) and 1,3-Diphenylpropane-2-^{14}C (1-2-^{14}C). The starting materials for these two isotope position isomers were phenylacetic-*2*-^{14}C acid and phenylacetic-*1*-^{14}C acid,[17] respectively, both of which were prepared through the carboxylation of benzylmagnesium chloride,[17] in which either the benzyl chloride or the carbon dioxide was labeled with carbon-14. The two acids were then reduced with lithium aluminum hydride to 2-phenylethanol-*2*-^{14}C and 2-phenylethanol-*1*-^{14}C. The 2-phenylethanols were converted into the bromides with HBr.[18] The Grignard reagents of each bromide were prepared by the following procedure: 2-phenethyl bromide (-*1*-^{14}C or -*2*-^{14}C) (25 g) was converted into 2-phenethylmagnesium bromide with 3.25 g of Mg in 200 mL of anhydrous ether. The reaction was stirred at room temperature 2 h after which benzaldehyde (14.2 g, previously purified) in 100 mL of ether was added slowly with stirring. The product was worked up as usual, and then distilled over 10 g of fused $KHSO_4$, yielding 1,3-diphenylpropene-*1*-^{14}C and 1,3-diphenylpropene-*2*-^{14}C (13 g), 55% of theory, bp 135 °C (1 mm).[19] The NMR spectrum was as follows: 2 H at 3.52 ppm (downfield from Me_4Si), 5.2-Hz splitting; 2 H at 6.42 ppm (complex multiplet); 10 H at 7.5 ppm (multiplet).

Each of the above isotope position isomers of 1,3-diphenylpropene-^{14}C (10 g) was dissolved in absolute ethanol (25 mL) and to the solution was added 2 g of Raney nickel catalyst.[15] The solutions were then hydrogenated in a Parr apparatus under 2-bar pressure of hydrogen until the reaction stopped. After removal of the catalyst and ethanol, distillation (125 °C (1 mm)) afforded 1,3-diphenylpropane-*1*-^{14}C or 1,3-diphenylpropane-*2*-^{14}C in near-quantitative yields. These preparations were carried out several times. The levels of radioactivity were 5–20 mCi/mol, and radioactive purity was established by GC traces (including ^{14}C monitor).

Phenetole-*α*-^{14}C and Phenetole-*β*-^{14}C (3-*α*-^{14}C and 3-*β*-^{14}C). Ethyl-*1*-^{14}C iodide[20] and ethyl-*2*-^{14}C iodide[21] were converted into **3**-*α*-^{14}C and **3**-*β*-^{14}C, respectively, through the Williamson synthesis.[22] The radioactivity levels were 5–20 mCi/mol.

***p*-Methylphenetole (Ethyl *p*-Tolyl Ether).**[23] The compound was prepared through the Williamson synthesis as described by Hickinbottom. The product was a clear liquid, bp 187–188 °C (Birosel[23] reports 186–188 °C). Purity was established through GC and NMR analyses.

***p*-Ethyltoluene.** *p*-Ethyltoluene has been described by Rossini.[24] We prepared it from *p*-tolualdehyde and methylmagnesium iodide to yield methyl-*p*-tolylcarbinol, which was reduced by zinc amalgam in aqueous HCl to yield *p*-ethyltoluene. Purity was demonstrated by GC and NMR analyses.

Reactions of Compounds 1–3 and Their Isotope Position Isomers with Tetralin at 400 °C. The reactant (phenetole, 1,3-diphenylpropane, or powdered vitrain from Illinois No. 6 coal) and tetralin (usually 1:1 by weight) were placed in stainless steel tubes (6 in. in length, ⅜ in o.d., 1/16 in. thick) equipped with compression-type Swage-Lok fittings. In our early experiments the tubes were placed in a preheated oven for the appropriate times, after which they were cooled by immersion in water. In later experiments a fluidized bed "TECAN SBL 2" was employed. No effort was made to exclude air, since preliminary experiments in which air was excluded revealed no significant differences from those experiments in which it was not. **1**-*1*-^{14}C and **1**-*2*-^{14}C, after the described treatment (see Table I), gave products which were analyzed by GC equipped with radioactivity monitor, and the traces are shown in Figures 6 and 7. From Figure 6 it is clear that both toluene and ethylbenzene are labeled but that the methylnaphthalenes are not. From Figure 7 we see that ethylbenzene and the methylnaphthalenes contain carbon-14, but that the toluene does not. In early experiments the toluene, ethylbenzene, and methylnaphthalenes were isolated and identified by their NMR spectra. **3**-*α*-^{14}C and **3**-*β*-^{14}C gave products which were similarly analyzed, and their traces are shown in Figures 8 and 9, respectively. Ethylene was identified as a constituent of the gaseous products from the reaction of **3** with tetralin; the ethylene so formed was brominated (vacuum line), and the 1,2-dibromoethane produced was isolated

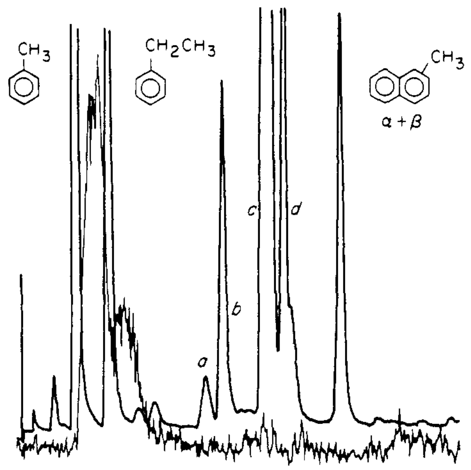


Figure 6. GC traces for product of reaction of 1-*1*-^{14}C with tetralin, 400 °C, 19 h. The weaker trace is for carbon-14. Peaks a, b, c, and d are indan, 1-methylindan, tetralin, and naphthalene, respectively.

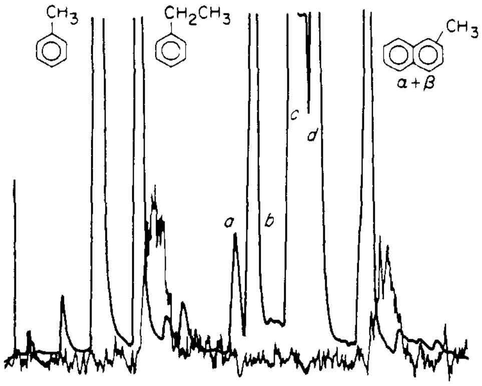


Figure 7. GC traces for product of reaction of 1-*2*-^{14}C with tetralin at 400 °C, 18 h. The weaker trace is for carbon-14. Peaks a, b, c, and d are indan, 1-methylindan, tetralin, and naphthalene, respectively.

and identified through its NMR spectrum. 1,3-Diphenylpropene was subjected to the same treatment in tetralin at 400 °C and the products were analyzed by GC.[9] The results are shown in Table I.

Crossover Experiments with Phenetole-α-^{14}C and Ethyl *p*-Tolyl Ether. The two reactants, prepared as described above (1.0 g each) were mixed with 2.0 g of tetralin and heated in the "TECAN SBL 2" fluidized bed bath at 400 °C for 41 h. The tube was cooled in water, opened, and poured into aqueous KOH solution. The mixture was stirred overnight, and the base-insoluble material was separated, washed, and subjected to GC and ^{14}C monitoring. *p*-Ethyltoluene was clearly nonradioactive. Ethylbenzene and *p*-xylene could not be completely resolved on the Barber-Coleman GC (75 °C isothermal, Dexsil 300); so the mixture was isolated (15% Dexsil 300, 8 ft × ¼ in., 60–325 °C (6°/min)) and then separated[9] (50 °C, 20% Apiezon N). The results are shown in Figure 10, and illustrate that, although the ethylbenzene is labeled, the *p*-xylene is not. *p*-Ethylbenzene from the crossover experiment was isolated in a similar way, and its NMR spectrum was compared with that of an authentic sample, prepared as described above.

Oxidation of Toluene-^{14}C and Ethylbenzene-^{14}C from Reaction of 3-α-^{14}C and 3-β-^{14}C with Tetralin at 400 °C. The samples were isolated by preparative GC, then oxidized with permanganate by the method of Slaugh[25] for the oxidation of ethyl-β-^{14}C-benzene. The results are shown in Figures 3 and 4.

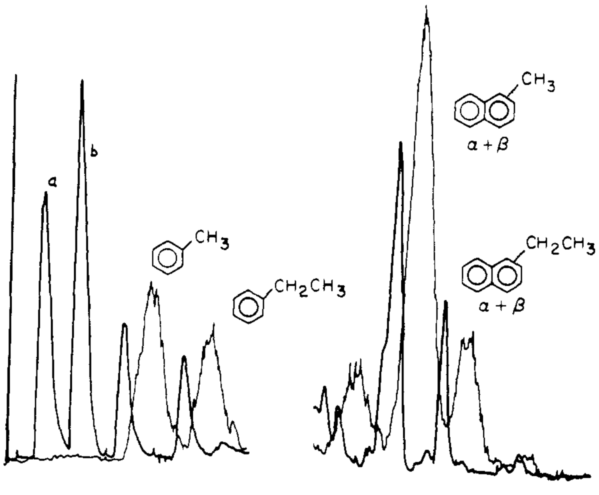


Figure 8. GC traces for the product of reaction of 3-α-^{14}C with tetralin at 400 °C, 18 h. The weaker trace is for carbon-14. Peaks a and b are acetone (solvent) and benzene, respectively.

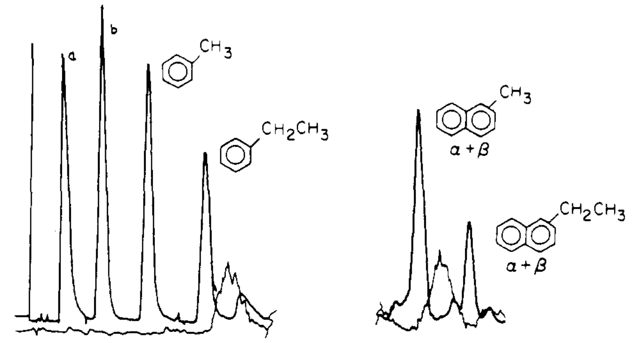


Figure 9. GC traces for the product of reaction of 3-β-^{14}C with tetralin at 400 °C, 18 h. The weaker trace is for carbon-14. Peaks a and b are acetone (solvent) and benzene, respectively.

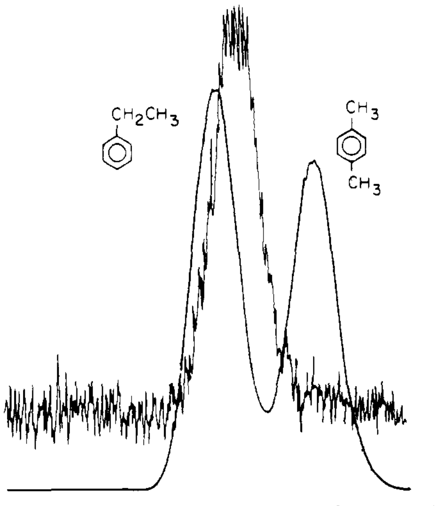


Figure 10. GC trace of ethylbenzene and *p*-xylene fraction isolated from crossover experiment.

Determination of Yields of β-Methylnaphthalenes Obtained by Treatment of Illinois No. 6 Vitrain with Tetralin-^{14}C at 400 °C. Tetralin-*1*-^{14}C[7] (1.33 g, 15.82 mCi/mol) was mixed with 2.0 g of Illinois No. 6 vitrain and heated at 400 °C for 24 h. The tube was cooled and washed with benzene. The solid residue was heated for 4 h with benzene and β-methylnaphthalene (100 mg), then cooled, and extracted with benzene. The two benzene fractions were combined. The methylnaphthalene was isolated by preparative GC (8 ft × 1/8 in. Dexsil, 50–300 °C (8°/min)). The foregoing conditions do not separate α- and β-methylnaphthalenes. Naphthalene and another fraction believed to contain ethylnaphthalenes were also isolated. NMR spectra confirmed the identities of the first two compounds—the third was shown to be a mixture. Radioactivity assay of methylnaphthalenes (5.642, 5.627 mCi/mol) allowed the calculation that the methylnaphthalenes represent 2.8% by weight of the vitrain. The solid fraction left after addition of β-methylnaphthalene and extraction with benzene was dried and assayed for carbon-14 (^{14}C equiv wt 2110, or 6.3% of tetralin-^{14}C retained). The solid sample was then heated at 80 °C for 1 h with an excess of tetralin. The filtered, dried solid (^{14}C equiv wt 2739) still retained 4.8% tetralin-^{14}C.

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Appendix

Derivation of Stoichiometric Equation for Reactions 1–9. Reactions 1–9 may be abbreviated as follows:

$$\underset{1}{\mathrm{PhCH_2CH_2CH_2Ph}} \rightarrow \underset{1}{\mathrm{PhCH_2\cdot}} + \underset{1}{\mathrm{\cdot CH_2CH_2Ph}}$$

$$\underset{1}{\mathrm{PhCH_2\cdot}} + \mathrm{tetralin} \rightarrow \underset{1}{\mathrm{PhCH_3}}$$

$$\underset{1-x}{\mathrm{PhCH_2CH_2\cdot}} + \mathrm{tetralin} \rightarrow \underset{1-x}{\mathrm{PhCH_2CH_3}}$$

$$\underset{x}{\mathrm{PhCH_2CH_2\cdot}} + \mathrm{tetralin} \rightarrow \underset{x}{\mathrm{C_{10}H_{11}CH_2CH_2Ph}}$$

$$\underset{x}{\mathrm{C_{10}H_{11}CH_2CH_2Ph}} \rightarrow \underset{x}{\mathrm{methylnaphthalenes}} + \underset{x}{\mathrm{PhCH_3}}$$

Assuming 1 mol of 1,3-diphenylpropane undergoes reaction, the phenylethyl radical distributes itself between reactions leading to ethylbenzene $(1 - x)$ and methylnaphthalenes and toluene (x). The total moles of product are thus $(2 + x)$, and the moles of toluene, ethylbenzene, and methylnaphthalenes formed per mole of reactant are, respectively $(1 + x)$, $(1 - x)$, and x.

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