planar $^+$NH bond and remaining lone pair), a rationalization for the anomalous Brønsted behavior could be provided, since steric and electronic interactions are considerably different in gauche and coplanar lone-pair conformations. Work designed to test these ideas is in progress.[9]

References and Notes

(1) (a) Evans, D. H.; Kinlen, P. J., unpublished work. (b) Kinlen, P. J., Ph.D. Thesis, University of Wisconsin, 1978. (c) The potential was stepped from a value where hydrazine is not oxidized to one where electron transfer is diffusion controlled, and the kinetic current (i_K) monitored as a function of time, comparing its value in the presence of an excess of acid, where the hydrazine is effectively all protonated, with the diffusion current (i_O) measured in the absence of acid. The presence of an oxidation wave attributed to the Hyd$^+\cdot$,A$^-$ ion pair precluded the use of usual pseudo-first-order deprotonation conditions (and use of acetonitrile even in the absence of an excess of A$^-$). The heterogeneous equivalent technique of Ružić and Feldberg[1d] was used to calculate a theoretical curve for i_K/i_D (ref 1b, pp 82–93; computer program, pp 216–218) which was followed well experimentally. For tetramethylhydrazine, the experimental values of k_b thus determined were observed to be constant to ±0.1 log unit over a hydrazine concentration range of 1.0–4.8 mM and a salicyclic acid concentration range of 50–200 mM (ref 1b, pp 139–146). The sensitivity of the rate constants to the concentration of water in the Me_2SO has not been explicitly tested, but the Me_2SO samples employed (ref 1b, p 80) have a residual water concentration of ~10 mM. (d) Ružić, I; Feldberg, S. *J. Electroanal. Chem.* **1974,** *50,* 153.

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(9) We thank the National Science Foundation for support of this work, under Grants CHE77-24627 and CHE78-08727.

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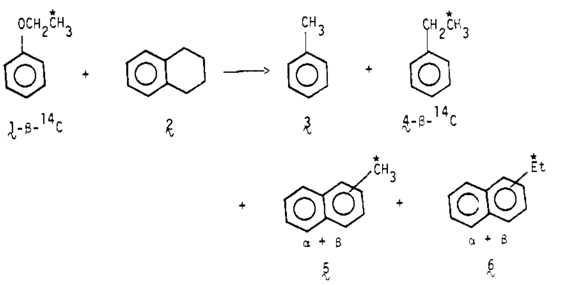
1,2 Shift of Phenyl from Oxygen to Carbon in a Free Radical[1]

Sir:

The importance of tetralin as a hydrogen donor in coal technology is well known,[2] and we recently reported on its reactions with Wyodak and with Illinois No. 6 vitrain, as well as with a series of model compounds.[3-5] We observed[4] that coal and tetralin-^{14}C when heated at 400 °C for 1 h yield traces of carbon-14-labeled α- and β-methylnaphthalenes. Since tetralin alone[5] yields no measurable amounts of methylnaphthalenes, we presume that the methyl groups in these compounds originate in the coal. Treatment of several aralkyl hydrocarbons and ethers with tetralin under the same conditions also yielded, among many other products, 4-10% methylnaphthalenes; experiments[4] with carbon-14-labeled hydrocarbons and ethers leave no doubt that intermolecular transfer of carbon occurs in the formation of the alkylnaphthalenes.

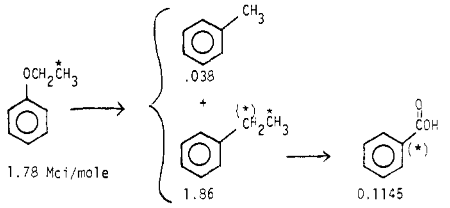
We report here on the reactions, with tetralin at 400 °C, of phenetole-α-^{14}C and phenetole-β-^{14}C.[6] In a typical run (18 h, 62% conversion) the yields, based on GC analyses were as follows: benzene, 11%; toluene, 11%; ethylbenzene, 11%; phenol, 47%; methylnaphthalenes, 16%; ethylnaphthalenes, 4%. Water was also formed. GC-MS analyses revealed[5] traces of other compounds. Monitoring of the radioactivity[7] of the toluene, ethylbenzene, and methyl- and ethylnaphthalenes from phenetole-α-^{14}C disclosed that these products contained carbon-14. An unexpected and surprising result from the reaction of phenetole-β-^{14}C (**1**-β-^{14}C) with tetralin (**2**) at 400 °C was the observation that the toluene (**3**) contained only a trace of carbon-14, whereas ethylbenzene (**4**) and the alkylnaphthalenes (**5** and **6**) were all labeled. The result for toluene was confirmed by its isolation and radioactivity assay.[8] The carbon-14 distribution in the ethylbenzene-^{14}C produced was determined after isolation by oxidation[9] to benzoic-^{14}C acid and carbon-14 determination.[8] The results are shown in Scheme I and were checked independently through similar experiments with phenetole-α-^{14}C.[10]



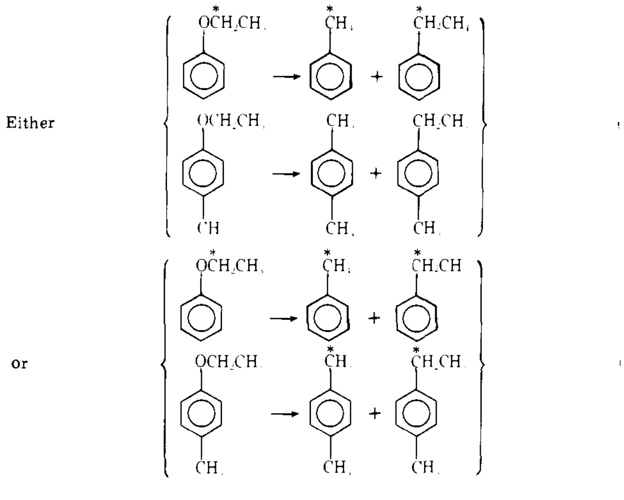
Although the alkylnaphthalenes (**5** and **6**) were formed through intermolecular reactions,[11] the mechanisms for the formation of **3** and **4** could, in principle, be either inter- or intramolecular. To resolve this question, we carried out the experiments outlined in Scheme II, in which a 50:50 mixture of phenetole-α-^{14}C and ethyl p-tolyl ether were heated with tetralin at 400 °C for 40 h. If toluene and ethylbenzene were formed by intramolecular processes, then only toluene and ethylbenzene should contain carbon-14, as shown in situation 1 in Scheme II. If the processes are intermolecular, then all four products should be labeled (2). The p-xylene and p-ethyltoluene produced were devoid[7] of radioactivity, signifying intramolecular processes.[12]

There are five conceivable pathways for the homolysis of phenetole; these yield the radical pairs A + B, C + D . . . J + K. Phenetole-β-^{14}C is portrayed to illustrate the carbon-14 distributions in the appropriate products (Scheme III). We recognize that C–H homolysis occurs through hydrogen ab-

Scheme I. Radioactivity Distributions in Toluene and Ethylbenzene Fractions Obtained from Heating Phenetole-β-^{14}C in Tetralin at 400 °C.



Scheme II. Results Expected for Crossover Reactions of Phenetole-α-^{14}C with ethyl p-tolyl ether in tetralin at 400 °C through intramolecular (1) or intermolecular (2) processes.



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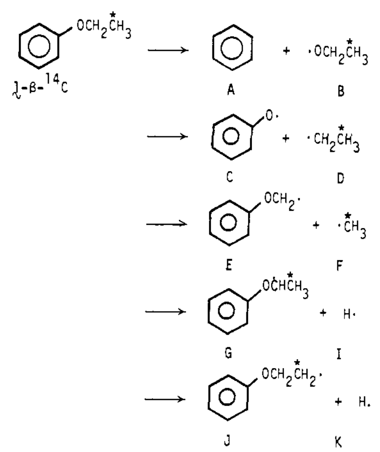
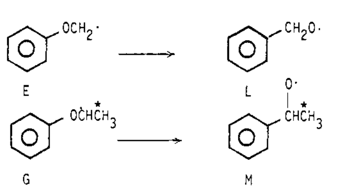
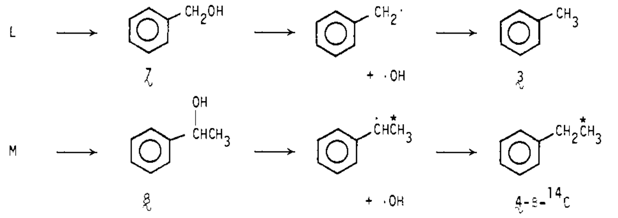
Scheme III



straction by another radical and that homolysis of **1** to A and B is energetically unfavorable. The phenyl radical A, in fact, is most likely formed by decomposition of E to A and formaldehyde.

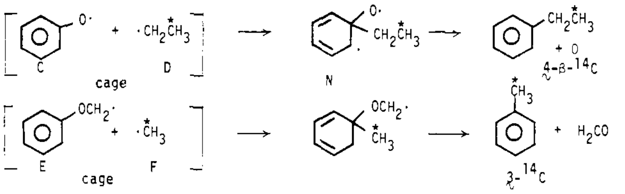
Benzene and phenol result from the abstraction of hydrogen atoms by A and C, respectively, from tetralin. Toluene (**3**) and ethylbenzene (**4**-β-^{14}C), however, must be produced through intramolecular migration of phenyl from oxygen to carbon in the intermediates E and G; the rearranged radicals L and M then convert into benzyl alcohol (**7**) and α-phenylethanol (**8**), respectively, which go on to **3** and **4**-β-^{14}C as shown. α-Phenylethanol (**8**) does, in fact, decompose under the conditions of the reaction to yield ethylbenzene and some toluene, as we showed in an independent experiment.



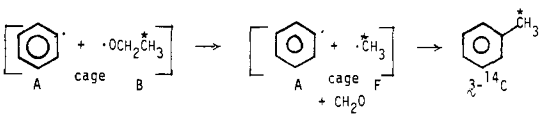


The α- and β-methylnaphthalenes (**5**) and α- and β-ethylnaphthalenes (**6**) are formed intermolecularly through pathways that are not as yet clear.

The fact that toluene (**3**) and ethylbenzene (**4**) are formed through intramolecular reactions (as demonstrated by the crossover experiments, Scheme II) precludes an ipso reaction.[13] A referee has suggested ipso attack by methyl or ethyl radicals from a cage. Such a mechanism has no precedent, would require in one case the expulsion of atomic oxygen, and would lead, in any event, to labeled toluene, contrary to our observation. Likewise, recombination of radicals formed in a cage (also suggested by the referee) should also lead to labeled toluene.



Cage formation at 400 °C near the critical temperature of tetralin is, in any event, highly unlikely.



Although 1,2 shift of phenyl from oxygen to carbon in a free-radical intermediate has been claimed,[14] the evidence is unconvincing and largely circumstantial. In the present work there can be little doubt that 1,2 shift occurs intramolecularly from oxygen to carbon through free-radical intermediates.[15]

Acknowledgment. The authors acknowledge helpful discussions with Dr. M. Poutsma, of Oak Ridge National Laboratory.

References and Notes

(1) Research sponsored by the Division of Chemical Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

(2) See, for example, the discussion of the Pott-Broche process by K. F. Schlupp and H. Wien, *Angew Chem., Int. Ed. Engl.*, **15**, 341-346 (1976).

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(6) Ethanol-*1*-^{14}C and ethanol-*2*-^{14}C were prepared from appropriately labeled sodium acetates according to A. Murray III and D. L. Williams, "Organic Syntheses with Isotopes", Part I, Interscience, New York, 1958, pp 905, 906. The labeled ethanols were converted to ethyl iodides (H. S. King, "Organic Syntheses", Collect. Vol. II, New York, 1943, p 399) and thence to phenetole-α-^{14}C and phenetole-β-^{14}C through the Williamson synthesis (W. J. Hickinbottom, "Reactions of Organic Compounds", Longmans, Green and Co., New York, 1948, p 91).

(7) A Barber-Coleman 5000 gas chromatograph fitted with radioactivity (carbon-14 and tritium) monitoring accessories was used.

(8) The dry combustion method with Borkowski ion chamber and vibrating reed electrometer was used. The method is described in Chapter 11, by V. F. Raaen, G. A. Ropp, and H. P. Raaen, "Carbon-14", McGraw-Hill, New York, 1968.

(9) The method used was that of L. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959).

(10) Phenetole-α-^{14}C was converted[5] to toluene-^{14}C and ethylbenzene-^{14}C (4.46 mCi/mol). Benzoic-^{14}C acid was obtained from toluene, 4.11 mCi/mol, and benzoic-^{14}C acid from ethylbenzene, 4.04 mCi/mol. The discrepancies with the data in Scheme I are due to isotope effects during the oxidations to benzoic acid. See, for example, W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, **75**, 2308 (1953).

(11) When phenetole and tetralin-*1*-^{14}C (C. J. Collins, *J. Am. Chem. Soc.*, **73**, 1038 (1951)) were heated at 400 °C, the alkylnaphthalenes were all of essentially the same carbon-14 content as the reactant tetralin-^{14}C.[7]

(12) The *p*-xylene was identified by its GC retention times and by admixture with an authentic sample. The *p*-ethyltoluene, however, was isolated by preparative GC (Varian Aerograph, Series 2800) and identified by NMR Varian XL-100. Radioactivity determinations were by GC fitted with a carbon-14 monitor.[7]

(13) See, for example, C. R. Everly and J. G. Traynham, *J. Am. Chem. Soc.*, **100**, 4316 (1978).

(14) M. F. R. Mulcahey, B. G. Tucker, D. J. Williams, and J. R. Wilmshurst, *Chem. Commun.*, 609-610 (1965). See also the review by J. W. Wilt, "Free Radicals", J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 8, pp 353-356.

(15) The carbon-14 (6%) found in the α position of ethylbenzene (Scheme I) is as yet unexplained. In this connection it is significant that, in an experiment in which anisole and tetralin were heated at 400 °C for 23 h, toluene and ethylbenzene were formed, among other products (GC analysis) in a ratio of ~4:1. See also J. W. Wilt and M. W. Stumpf, *J. Org. Chem.*, **30**, 1256 (1965).

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The Nonclassical Brexyl Cation. A Reassessment[1]

Sir:

In two recent papers,[2,3] the Blys and co-workers reported results of solvolyses of deuterium- and carbon-13-labeled β-

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