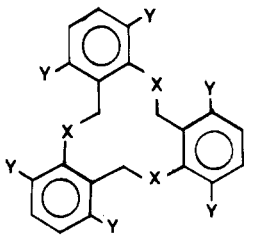
disagreement with the force field calculations. At room temperature significant amounts of the saddle may well be present.[24]

The all-s-trans geometry which has been suggested as the likely conformation for 1 by Untch and Martin[2] is the same as our helix conformation. Similar conformations have also been reported for the trithia (**2a**)[6] and 3,6-dimethyl (**2b**)[5] derivatives of tribenzo-1,5,9-cyclododecatriene (**2c**). However, the barriers for the pseudorotation of the helix conformations of **2a** and **2b** are 9.3 and 17.1 kcal/mol, respectively, which are considerably higher than that observed in 1 (5.9 kcal/mol). On the other hand, the difference between the strain energies of the propeller and helix conformations of **2b** has been calculated to be 0.9 kcal/mol,[5] as compared to 7.8 kcal/mol for the corresponding conformations of 1.



2a, X = S; Y = H
2b, X = CH_2; Y = CH_3
2c, X = CH_2; Y = H

Although the propeller conformation is unfavorable in the systems discussed above, such is not the case in compounds where the CH_2CH_2 units in the tribenzo-1,5,9-cyclododecatriene **2c** are replaced by three ester or amide groups.[7]

Acknowledgment. This work was supported by the National Science Foundation.

Registry No. 1, 4736-48-5.

(24) The helix has C_2 symmetry and is chiral whereas the saddle has no real axes of symmetry and is chiral. Furthermore, the saddle is more flexible than the helix. Thus the saddle should be favored over the helix by at least R ln 2 (1.4 eu), and at room temperature the helix and saddle are calculated to have closely comparable free energies.

Radical Pathways of Coal Dissolution in Hydrogen Donor Media. 2.[1a] β Scission and 1,2 Aryl Migration Reactions of Radicals Derived from Methylindans and Tetralin at 327–627 °C[1b]

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The 1,2 aryl migration and fragmentation reactions of 1-indanylmethyl (1), 2-tetralyl (2), 2-indanylmethyl (3), 1-tetralyl (4), 2-methyl-1-indanyl (5), and 1-methyl-2-indanyl (6) radicals were studied by flash vacuum pyrolysis of the *tert*-butyl perester precursors at 327–627 °C and 10^{-2} torr. Radicals 1 and 2 are interconverted via a 1,2 aryl migration which is readily reversible at all temperatures. This equilibrium is depleted by β scission of 1 and recyclization to 4 and by β scission of 2 followed by recyclization to 2 or to 3 in modest yields. The reverse neophyl-like rearrangement of 2 to 1 occurs with a lower activation barrier than β scission of 1 to form a 2-(*o*-vinylphenyl)ethyl radical. Enthalpies, entropies, and free energies of reaction were calculated for the above reactions from group additivity parameters, and activation energies were estimated from values reported for simple alkyl radicals. It is shown that the β scission of 4 and recyclization to 1 is important only at very high temperatures (>500 °C) as a mechanism for the isomerization of tetralin and related hydroaromatic structures to alkylindans and that the reverse neophyl-like rearrangement of 2 to 1 is the favored pathway for isomerizations observed during dissolution of coal in hydroaromatic media at elevated temperatures.

The conversion of coal to soluble products is accomplished by heating coal in a hydroaromatic solvent, occasionally under hydrogen pressure, at 400–475 °C for periods of from seconds[2] to a few minutes.[3] Model compound studies have sought to identify coallike organic structures which undergo decomposition on the time scale of coal dissolution.[4] Thermal production of radicals during the dissolution process provides coal-derived radicals which can undergo β scission, addition to available aromatic systems, disproportionation, combination, and hydrogen abstraction either from a hydroaromatic or aliphatic structure in the coal or from the hydroaromatic solvent. The hydroaromatic solvent undergoes isomerization and fragmentation along with oxidation to the corresponding aromatic structure. When tetralin is used as a solvent, *n*-butylbenzene, indan, 1-methylindan, *cis*- and *trans*-decalin, 1,2- and 1,4-dihydronaphthalene, and methylnaphthalenes are minor products, naphthalene and tetralin comprising the major solvent-derived products.[2] Analogous results have been observed with octahydrophenanthrene.[5]

(1) (a) Paper 1 in this series: James A. Franz and Donald M. Camaioni, *Fuel*, **59**, 803 (1980). Preliminary accounts of this work were presented at the 178th National Meeting of the American Chemical Society, Washington, DC, Sept 1979, Abstract ORGN 205, and the 1979 Materials Research Society Annual Meeting, Symposium H. (b) This work was supported by the U.S. Department of Energy, Processes and Techniques Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, under contract DE-AC06-76RLO-1830, with Battelle Memorial Institute.

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(3) R. C. Neavel, *Fuel*, **55**, 237 (1976).

(4) Ben M. Benjamin, Vernon F. Raaen, P. H. Maupin, L. L. Brown, and C. J. Collins, *Fuel*, **57**, 269 (1978).

(5) (a) D. C. Cronauer, D. M. Jewell, Y. T. Shah, and R. J. Modi, "Investigation of Mechanism of Hydrogen Transfer in Coal Hydrogenation, Phase I Final Report", under DOE Contract No. E(49-18)-2305, Feb 1978; (b) Yatish Y. Shah, and Donald C. Cronauer, *Catal. Rev.—Sci. Eng.*, **20**, 209 (1979).

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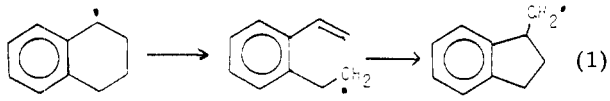
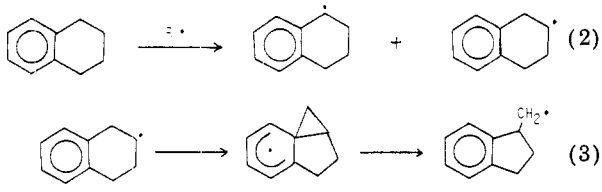
Radical mechanisms for the isomerization of tetralin have been suggested. Curran[6] attributed the formation of methylindan to the β scission of 1-tetralyl and recyclization to 1-indanylmethyl followed by hydrogen abstraction to form 1-methylindan (eq 1). Benjamin et al.[7]



(1)

studied the pyrolysis of tetralin-*1*-^{13}C at 500 °C and found the product 1-methylindan to have 45% of the label in the 3-position, 48% in the methyl, 2% in the 2-position, and 5% in the 1-position. We presented evidence[1] that coal-derived radicals are sufficiently nonselective to produce 2-tetralyl as well as 1-tetralyl in hydrogen abstraction reactions during the dissolution of coal at 427 °C. Contrary to the suggestion of Curran, the major pathway of isomerization is thus consistent with the reverse neophyl-like rearrangement of 2-tetralyl radical to 1-indanylmethyl (eq 2).



(2)

(3)

The neophyl-like rearrangement as studied in solution usually occurs to form only the more stable radical.[8] Evidence of reversibility exists for interconverting radicals of equivalent stability[9] and in perhaps one case for interconverting radicals of differing stabilities.[10] From the tetralin thermolysis studies it would appear that at elevated temperatures the neophyl rearrangement is reversible and that unimolecular fragmentations such as β-scission reactions may also occur.

In previous coal-related studies of isomerization and fragmentation of hydroaromatic systems, identities of radical intermediates were not established. In this paper, we apply the method of flash vacuum pyrolysis (FVP) of perester radical precursors to examine the reversible 1,2 aryl migration of 2-tetralyl and 1-indanylmethyl. Also we study the β-scission/recyclization reactions of 1-indanylmethyl to 1-tetralyl and of 2-indanylmethyl to 2-tetralyl and the methyl radical β-scission reactions of 1-methyl-2-indanyl and 2-methyl-1-indanyl radicals. These reactions represent principal pathways of isomerizations of hydroaromatic systems and alkyl group cleavage during coal dissolution. Thermochemical data for the reactions are calculated by group additivity methods[11,12] to illustrate thermodynamically favored pathways of rearrangements, and activation barriers for rearrangements and fragmentations are estimated on the basis of this data and on available data from simple alkyl radical fragmentations.

(6) G. P. Curran, R. T. Struck, and E. Gorin, *Ind. Eng. Chem. Process Des. Dev.*, 6, 166 (1967).
(7) Ben M. Benjamin, Edward M. Hagaman, Vernon F. Raaen, and Clair J. Collins, *Fuel*, 58, 386 (1979).
(8) James W. Wilt in "Free Radicals", Vol. I, Jay K. Kochi, Ed., Wiley-Interscience, New York, 1973, pp 334–501.
(9) L. H. Slaugh, *J. Am. Chem. Soc.*, 81, 2262 (1959); W. A. Bonner and F. D. Mango, *J. Org. Chem.*, 29, 29 (1964).
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(11) Sidney W. Benson, "Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters", Wiley, New York, 1968.
(12) H. Edward O'Neal and Sidney W. Benson in "Free Radicals", Vol. II, Jay K. Kochi, Ed., Wiley-Interscience, New York, 1973, pp 275–359.

Table I. Flash Vacuum Pyrolysis Products of *tert*-Butyl 1-Methylindan-2-percarboxylate

	product distrib, % of total			
products	327 °C	427 °C	527 °C	627 °C
indene	48.8	72.8	78.7	81.7
1-methylindan	11.1	4.99	4.15	2.70
3-methylindene	7.44	2.13	1.95	2.15
1,2-dimethylindan[a]	23.4	9.55	4.93	3.05
1-methylindene	7.45	8.61	9.41	8.76
methyl 1-methylindan-2-carboxylate[b]	0.20	0.13	0.13	>0.1
1-methyl-2-*tert*-butoxyindan[b]	1.23	0.90	0.80	0.43

[a] Combined yields of cis and trans isomers. [b] Assigned on the basis of the similarity of GC retention times to those of 1-*tert*-butoxytetralin and methyl tetralin-1-carboxylate standards and on the basis of similarity of retention time of 1-*tert*-butoxy-2-methylindan (Table II).

Table II. Flash Vacuum Pyrolysis Products of *tert*-Butyl 2-Methylindan-1-percarboxylate

	product distrib, % of total			
products	327 °C	427 °C	527 °C	627 °C
indene	2.85	24.7	51.5	64.9
2-methylindan	9.38	9.9	3.0	1.6
1,2-dimethylindan[a]	33.1	24.2	12.3	7.1
2-methylindene	19.1	18.3	12.8	11.9
2,2'-dimethyl-1,1'-biindan[b]	12.9	8.7	4.4	0.8
1-*tert*-butoxy-2-methylindan[a]	14.0	10.0	10.2	8.1
methyl 2-methylindan-1-carboxylate	5.4	4.2	4.0	2.1

[a] Combined yields of cis and trans isomers. [b] Four GC peaks were observed for the eight possible diastereomers (two meso and six *d,l* pairs). All peaks gave identical mass spectral fragmentation patterns consistent with this structure.

Table III. Flash Vacuum Pyrolysis Products of *tert*-Butyl 1-Indanperacetate

	product distrib, % of total		
products	427 °C	527 °C	627 °C
indene	0.28	1.33	2.83
2-methylindan	0.45	0.28	0.16
1-methylindan	3.25	2.55	1.83
3-methylindene	0.21	0.52	1.14
1,3-dimethylindan	0.37	0.49	0.17
1-methylindene	0.84	2.69	4.45
1-methyleneindan	1.17	1.14	1.43
2-methyleneindan	<0.1	0.40	0.80
1-ethylindan	1.22	0.57	<0.1
tetralin	26.1	17.9	4.45
1,2-dihydronaphthalene	26.0	46.5	68.5
1,4-dihydronaphthalene	4.74	2.93	2.48
2-methyltetralin	5.64	2.24	0.81
1-methyltetralin	16.2	14.3	4.29
naphthalene	0.25	1.43	2.37
1,1'-bitetralyl	7.72	0.56	0.27
others[a]	5.5	4.1	3.1

[a] Includes intermediate to long retention time GC peaks (2.5% yield) some of which exhibit mass spectra and GC retention times consistent with those expected for *tert*-butoxy derivatives of tetralin, 1-methylindan, and methyl 1-indanacetate.

Results

Flash vacuum pyrolysis is a useful method for observing unimolecular radical reactions which are not normally

Table IV. Flash Vacuum Pyrolysis Products of *tert*-Butyl Tetralin-2-percarboxylate

products	product distrib, % of total 427 °C	527 °C	627 °C
indene	0.25	0.25	2.47
2-methylindan	0.42	0.24	0.13
1-methylindan	2.33	1.80	1.11
3-methylindene	0.25	0.49	1.18
1,3-dimethylindan	0.29	0.27	0.20
1-methylindene	0.70	2.26	4.52
1-methyleneindan	0.34	0.51	0.67
2-methyleneindan	0.10	0.38	0.81
1-ethylindan	0.65	0.26	<0.1
tetralin	28.4	20.9	10.5
1,2-dihydronaphthalene	29.3	48.4	66.5
1,4-dihydronaphthalene	6.02	4.87	2.74
2-methyltetralin	4.75	1.90	0.88
1-methyltetralin	12.7	9.75	3.93
naphthalene	0.27	0.51	2.91
1,1'-bitetralyl	8.30	3.68	0.28
other[a]	4.9	3.5	1.1

[a] Includes intermediate to long retention time GC peaks (1.5% yield) which exhibit mass spectra and GC retention times consistent with those expected for *tert*-butoxy derivatives of tetralin and 1-methylindan and methyl 1-indanacetate.

Table V. Flash Vacuum Pyrolysis Products of *tert*-Butyl 2-Indanperacetate

products	product distrib, % of total 327 °C	427 °C	527 °C	627 °C
indene	1.16	1.28	2.50	3.98
2-methylindan	21.4	10.4	6.80	4.59
1-methylindan	1.60	1.36	1.03	0.60
3-methylindene	0.16	0.21	0.63	1.11
1,2-dimethylindan (cis and trans)	1.32	0.76	0.38	0.20
1,3-dimethylindan (cis and trans)	1.33	1.28	1.42	1.65
1-methylindene	0.14	1.19	3.04	4.55
1-methyleneindan	0.31	0.10	0.19	0.32
2-methyleneindan	<0.05	0.17	0.60	1.08
1-ethylindan[a]	<0.5	<0.5	<0.5	<0.5
2-ethylindan	10.9	4.55	1.91	0.95
tetralin	20.1	17.7	11.2	6.66
1,2-dihydronaphthalene	15.0	29.7	49.8	60.8
1,4-dihydronaphthalene	3.78	3.17	2.33	0.75
2-methyltetralin	7.22	2.71	0.86	0.32
1-methyltetralin	10.1	19.7	13.7	4.84
naphthalene	0.33	0.44	1.70	6.15
1,1'-bitetralyl	0.58	0.62	0.22	<0.05
other[b]	4.3	4.1	1.6	1.45

[a] Small amounts partially resolved (small shoulder) from 2-ethylindan in the GC. [b] Unidentified GC peaks, some of which have retention times consistent with *tert*-butoxy derivatives and methyl 2-indanacetate.

observable in solution reactions. The method achieves a desired temperature essentially instantaneously, and choice of operating pressure allows unimolecular rearrangements and fragmentations to compete with diffusion-controlled radical combination and disproportionation.[13] This permits relatively high energy reactions to be observed and associated with a known precursor radical.

In this work, *tert*-butyl peresters were used as radical precursors because of their efficient decomposition at 327–627 °C and sufficient volatility at 10^{-2} torr. Thus, the desired alkyl radical was produced in the presence of methyl radical from β scission of *tert*-butoxy (eq 4 and 5).

$$R\text{-}CO_2\text{-}OC(CH_3)_3 \rightarrow R\cdot + CO_2 + (CH_3)_3CO\cdot \quad (4)$$

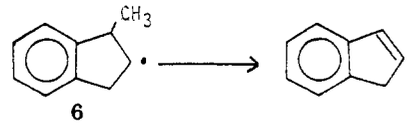
$$(CH_3)_3CO\cdot \rightarrow (CH_3)_2CO + CH_3\cdot \quad (5)$$

Table VI. Flash Vacuum Pyrolysis Products of *tert*-Butyl Tetralin-1-percarboxylate

products	product distrib, % of total 427 °C	527 °C	627 °C
indene	<0.05	0.29	1.48
1-methylindan	0.05	0.13	0.12
3-methylindene	<0.05	0.10	0.60
1-methylindene	<0.05	0.63	2.40
1-methyleneindan	<0.05	0.11	0.45
tetralin	13.5	11.9	6.13
1,2-dihydronaphthalene	33.9	47.9	69.5
1,4-dihydronaphthalene	<0.05	0.73	1.26
1-methyltetralin	24.4	15.9	5.95
1-*tert*-butoxytetralin	20.0	17.8	10.1
methyl tetralin-1-carboxylate	1.51	1.05	0.33
1,1'-bitetralyl	4.75	2.61	0.36
unidentified compounds	1.94	0.85	1.34

The products (Tables I–VI) are those expected from radical combination and disproportionation reactions. The product distributions reflect the competition between diffusion-controlled radical-depletion reactions and intramolecular rearrangements. In general, all of the products are those formed from the initial decomposition of the perester followed by rearrangement and trapping by methyl or another alkyl radical. The production of secondary radicals by hydrogen abstraction from products appears to be only a minor pathway. As temperatures are increased, disproportionation products increase relative to combination products. The larger alkyl radicals form combination products with methyl but form only traces of dimers (e.g., 2,2'-bitetralyl), except for the benzylic-type alkyl radicals (e.g., 1,1'-bitetralyl and 2,2'-dimethyl-1,1'-biindan). In certain cases (2-tetralyl, 1-indanylmethyl), identical product distributions are obtained from either radical precursor. As discussed below, this is evidence for establishment of an equilibrium between interconverting radicals. The product distributions obtained from the peresters allow one to rank the relative energetics of the various β scissions and neophyl-like rearrangements and reveal which interconversions, occurring simultaneously with others, are readily reversible. For the various peresters, the results were as follows.

(A) *tert*-Butyl 1-Methylindan-2-percarboxylate. Table I summarizes the yields of products from the flash vacuum pyrolysis of this perester from 327 to 627 °C. The resulting 1-methyl-2-indanyl radical (**6**) undergoes β scission of methyl radical to produce indene, the major product, in 49–82% yield (eq 6). The remaining products

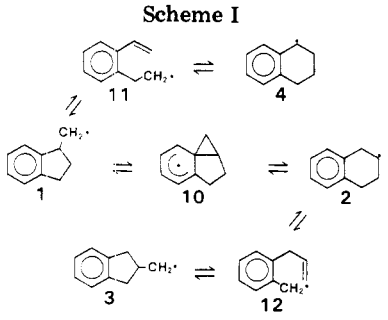


6 (6)

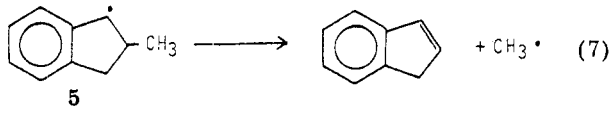
occur via disproportionation (1-methylindan, 3-methylindene, and 1-methylindene) or via combination with methyl radical (*cis*- and *trans*-1,2-dimethylindan). The reaction is very clean, with 99% absolute yield of products and no evidence for second-generation radical products (absence of 2-methylindan, 2-methylindene, or trimethylindan). No dimeric indan products were observed.

(13) For a discussion and leading reference dealing with gas-phase pyrolysis, see Sidney W. Benson and G. Neil Spokes, *J. Am. Chem. Soc.*, 89, 2525 (1967).

Scheme I



(B) *tert*-Butyl 2-Methylindan-1-percarboxylate. Table II summarizes the yields of products from the flash vacuum pyrolysis of the perester from 327 to 627 °C. This reaction is also relatively clean with high recovery of products. The formation of indene from 2-methyl-1-indanyl (eq 7) shows a greater temperature dependence



(7)

than that with 1-methyl-2-indanyl radical, varying from 3% to 65% at 327–627 °C. Indene was formed by the β scission of methyl radical, 2-methylindene and 2-methylindan were formed by disproportionation, and 1,2-dimethylindans were formed by methyl combination. Significant yields of isomers of 2,2′-dimethyl-1,1′-biindan were also detected.

(C) *tert*-Butyl 1-Indanperacetate. Products from the flash vacuum pyrolysis of this perester are listed in Table III. Substantial overall conversion to tetralin products occurs, consistent with the expected forward neophyl-like rearrangement. However, the presence of 1-tetralyl-derived products suggests that the β scission/recyclization of 1-indanylmethyl (the reverse of eq 1) occurs in competition with the 1,2 aryl migration. It will be noted that in the flash vacuum pyrolysis in part A no benzylic dimers (from secondary attack on products) were detected as well as no 1,1-dimethylindan. Thus, it is unlikely that the 1-tetralyl-derived products observed here in substantial yields occur via second generation attack on the product tetralin. There is also a small yield of 2-methylindan. This product presumably occurs via β scission of 2-tetralyl radical to give 2-allylbenzyl radical followed by recyclization to 2-indanylmethyl radical (see Scheme I) since 2-methylindan was not formed by methyl addition to indene during pyrolysis experiments in part A. Secondary radical reactions with products occur to a small extent as evidenced by two products, naphthalene and indene. Naphthalene results from hydrogen abstraction from 1,2- or 1,4-dihydronaphthalene followed by disproportionation, and indene probably forms via hydrogen abstraction from 2- or 1-methylindan at the 1- or 2-position followed by β scission of methyl radical. Finally, small yields of *tert*-butoxy adducts and methyl esters (listed under "other" products in Table III) were detected. These products may reflect a small degree of perester decomposition (<5%) in the reservoir leading to cage products (ethers and esters).

(D) *tert*-Butyl Tetralin-2-percarboxylate. The products and yields from this perester (Table IV) are similar to those of *tert*-butyl 1-indanperacetate. This indicates that 1-indanylmethyl and 2-tetralyl are rapidly interconverted relative to radical-depletion reactions. The yield of 1-indanylmethyl products increases with higher temperatures as predicted by $\Delta G°$ values from 5.2% at 427 °C to 11% at 627 °C. The yields of disproportionation products increase relative to combination products with increasing temperature. For example, the dihydronaphthalenes increase from 35% to 69% while methyltetralins and bitetralyl decrease from 26% to 15%. At 427 °C, a 13% yield of 1-methyltetralin and an 8% yield of bitetralyl show that at least 21% of the products form from β scission of 1-indanylmethyl and recyclization to 1-tetralyl. The 58% yield of tetralin and 1,2-dihydronaphthalene can arise from either 1-tetralyl or 2-tetralyl. The predominance of 1-methyltetralin over 2-methyltetralin suggests that a substantial but uncertain fraction of the 58% can be apportioned to 1-tetralyl. The results imply that the β scission of 1-indanylmethyl occurs at a slower rate than either the forward or reverse rates of interconversion of 2-tetralyl and 1-indanylmethyl, since the yields of 1-tetralyl products are identical starting with either precursor.

(E) *tert*-Butyl 2-Indanperacetate. Table V indicates that the 2-indanylmethyl radical undergoes efficient β scission/recyclization leading to tetralin and 1-methylindan products from a subsequent reverse 1,2 aryl migration of 2-tetralyl (see Scheme I). The degree of rearrangement to tetralin and related products increases from 61% to 85% over the range 327–627 °C. No open-chain products from the capture of β-scission intermediates were observed. Since the product distribution is not identical with those formed in experiments C and D above, we conclude that β scission of this radical is slower than interconversion of **1** and **2**. ΔG_{700} for the conversion of 2-indanylmethyl to 2-tetralyl (−8.02 kcal/mol) predicts an equilibrium distribution of products close to that of 1-indanylmethyl/2-tetralyl. The observed yields of all 2-methylindan and related products, 34%, shows that only partial conversion to the expected product distribution (assuming completely nonselective product formation) has occurred. The presence of 2-methyltetralin, 1-methylindan, and 1-methyltetralin shows that β scission of **3** occurred followed by recyclization to **2**, neophyl rearrangement of **2** to **1**, and β scission/recyclization of **1** to **4**.

(F) *tert*-Butyl Tetralin-1-percarboxylate. Table VI shows the products from the 1-tetralyl radical precursor. Partial decomposition of the perester in the reservoir during the experiment led to increased yields of the cage products, 1-*tert*-butoxytetralin and methyl tetralin-1-carboxylate. In order to make certain that a substantial percentage of perester was decomposing in the hot zone of the reactor, we determined the rate of decomposition of the neat perester at 40 °C by high-pressure LC. The perester was 50% decomposed at 4.0 h whereas flash vacuum pyrolysis experiments were completed in less than 2 h. At 427 °C only trace yields of products identified with 1-indanylmethyl or 2-tetralyl radicals were detected. However, yields of rearranged products of 1% at 527 °C and 5% at 627 °C were detected. The presence of 2-tetralyl radical is indicated by the small yield of 1,4-dihydronaphthalene, trace amounts of 2-methyltetralin are found, and the presence of 1-indanylmethyl is indicated by its disproportionation products. The decreasing yields of 1-*tert*-butoxytetralin may reflect partial decomposition of the ether at increasing temperatures.

Thermochemical Properties. Enthalpies, entropies, heat capacities, and free energies of formation for radicals (Table VII) were calculated by following the method of Benson.[11,12] On the basis of this data, enthalpies, entropies, and free energies of radical rearrangements were estimated (Table VIII).

Discussion

The objective of the present study is to establish a mechanistic pathway to explain the observed isomerization of tetralin and hydrogenated phenanthrenes to 1-

Table VII. Thermochemical Values for Radicals Calculated from Group Additives[13]

radical	$\Delta H_f^\circ{}_{300}$ [d]	S_{300}° [e]	C_p° [e] 300 K	500 K	800 K	1000 K
1-tetralyl	36.13	74.35	31.78	53.60	72.61	79.98
2-tetralyl	48.97	90.87	37.48	61.55	82.98	91.52
1-indanylmethyl	55.72	94.14	35.65	59.03	80.76	89.52
2-indanylmethyl	54.89	92.74	35.65	59.03	80.76	89.52
2-methyl-1-indanyl	38.55	90.37	35.31	59.01	81.23	90.12
1-methyl-2-indanyl	52.72	94.67	35.51	58.71	80.17	89.32
2-(*o*-vinylphenyl)ethyl	69.79	105.84	40.81	62.03	81.31	89.45
o-allylbenzyl	59.35	105.32	39.87	61.32	81.32	89.92
methyl	34.2[a]	46.4[b]	8.3[b]	10.1[b]	12.6[b]	14.0[b]
1,1-dimethyl-2-phenylethyl	40.43					
1,1-dimethylspiro[2.5]octa-4,7-dien-6-yl (**8**)	51.8[c]					
2-methyl-2-phenylpropyl	34.7					
tricyclo[4.4.0.0^{1,9}]deca-2,5-dien-4-yl (**10**)	68.8[c]					

[a] Experimental value: D. M. Golden and Sidney W. Benson, *Chem. Rev.*, **69**, 125 (1969). [b] Calculated by difference method estimates.[14] [c] Calculated from the estimated ΔH° of the hydrocarbon by using DH° = 69.8 kcal/mol for the cyclopentadienyl H atoms. The hydrocarbon ΔH° estimate requires the ΔH° contribution of C-(Cd)$_2$(*H*)$_2$ = 0.6 kcal/mol (Professor Sidney W. Benson, private communication). [d] In units of kcal/mol. [e] In units of cal/(mol deg).

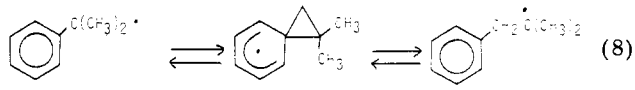
Table VIII. Thermochemical Values[a] for Radical Reactions Calculated by Group Additives[13]

reaction	ΔH_{300}°	ΔS_{300}°	ΔG_{300}°	ΔC_p° 300 K	400 K	500 K	600 K	800 K	1000 K
1 ⟶ 2	−6.75	−3.27	−5.77	2.22	2.22	2.22	2.22	2.22	2.22
11 ⟶ 1	−14.07	−11.7	−10.56	−5.16	−3.89	−3.00	−1.96	−0.55	+0.07
11 ⟶ 4	−33.66	−31.50	−24.21	−8.81	−8.81	−8.81	−8.81	−8.81	−8.81
12 ⟶ 3	−4.46	−14.45	−0.13	−4.22	−2.92	−2.29	−1.52	−0.46	−0.40
12 ⟶ 2	−10.38	−12.58	−6.61	−2.39	−0.79	0.23	0.73	1.66	1.60
6 ⟶ indene + methyl	23.85	5.41	22.23	−5.53	−3.85	−2.55	−1.64	−0.69	−0.10
5 ⟶ indene + methyl	37.52	9.71	34.61	−5.73	−3.75	−2.30	−1.19	−0.37	0.90

[a] Units of kcal/mol (ΔH°) and cal/(mol deg) (ΔS° and ΔC_p°).

methylindan and analogous phenanthrene-based products and to determine the favored pathway of dealkylation of 1-methylindan to indan, all of which occur during the reductive thermolysis of coal in hydroaromatic media. Little is known about the rates of formation of radicals, of steady-state concentrations of radicals, or of the degree of radical chain-induced decompositions of alkyl structures during coal dissolution at 400–500 °C in tetralin or other hydroaromatic media. Specific knowledge of radicals and mechanisms leading to structural isomerization and fragmentation in the highly aromatic and phenolic coal reaction medium is a first necessary step in understanding the suite of reactions which affect coal dissolution.

Reverse 1,2 Aryl Migration of 2-Tetralyl. Maillard and Ingold[14] have determined rate constants for several forward 1,2 aryl migrations. For the forward neophyl rearrangement, k = 59 s^{-1}, log A = 11.7, and E_a = 13.6 kcal/mol at 25 °C. Unlike 1,2 alkyl and 1,2 hydrogen atom migrations (none of which have been observed[8]) in which the partially migrated alkyl moiety would impart antibonding character to the transition state analogous to the exchange-forbidden equilateral triangle approach of an alkyl radical to an olefin,[15-17] the bridging aryl group is generally accepted to stabilize the transition state in the neophyl rearrangement.[18] The bridged intermediate in the neophyl rearrangement is thought to be in a very shallow well or no well from the absence of CIDNP polarization of the aromatic protons of cage products from the diacyl peroxide precursor to **7**[19] and the absence of hyperfine interaction with aromatic protons in the ESR spectra of **7** and **9**.[20] For the forward neophyl rearrangement of **7** to **9**, ΔH°_{298} = 6.9 kcal/mol (eq 8).[21]

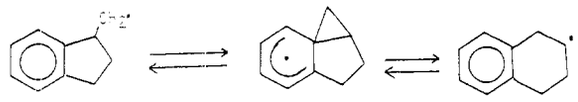


7 8 9 (8)

Combined with Maillard and Ingold's value of E_a, the reverse neophyl rearrangement should proceed with E_a = 20.5 ± 2 kcal/mol (or 21.6 kcal/mol by using Hamilton's value of ΔH° = 8 kcal/mol).[23] The enthalpy of formation of 8 can be estimated to be 51.8 ± 2 kcal/mol from $\Delta H_f^\circ{}_{298}$ of 1,1-dimethylspiro[2.5]hexa-4,7-diene (34.1 kcal/mol by group additivity[11]) by assuming a C–H bond dissociation energy of the parent spiro hydrocarbon equal to that of 1,4-cyclohexadiene, 69.8 kcal/mol.[24] Comparing the difference in enthalpy of **7** and **8** with E_a = 13.6 kcal/mol, we conclude that **8** lies in a 2.2 ± 3 kcal/mol well.[25] As

(14) B. Maillard and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 1224 (1976).
(15) K. Yamaguchi, *Chem. Phys. Lett.*, **28**, 93 (1974).
(16) V. Bonacic-Koutecky, J. Koutecky, and L. Salem, *J. Am. Chem. Soc.*, **99**, 842 (1977).
(17) Michael J. S. Dewar and Santiago Olivella, *J. Am. Chem. Soc.*, **100**, 5290 (1978).
(18) H. E. Zimmerman, "Molecular Rearrangements", Vol. I, P. de-Mayo, Ed., Wiley-Interscience, New York, 1973, pp 416–423.
(19) Phillip B. Shevlin and Hugh James Hansen, *J. Org. Chem.*, **42**, 3011 (1977). These authors show that the spiro intermediate has a lifetime of $<10^{-10}$ s, which places an upper limit of 6 kcal/mol on the barrier for ring opening of 8 at 105 °C.
(20) (a) D. J. Edge and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 7695 (1972); (b) A. Hudson and H. A. Hussain, *J. Chem. Soc. B*, 793 (1969); (c) A. Ohno, N. Kito, and Y. Onishi, *Bull. Chem. Soc. Jpn.*, **44**, 470 (1971).
(21) Enthalpies of formation of **7** (41.6 ± 1 kcal/mol) and **9** (34.7 ± 1 kcal/mol) were estimated by using enthalpies of formation of the hydrocarbons[22] and bond dissociation energies of 99 ± 1 and 91 ± 1 kcal/mol for the respective hydrocarbon C–H bonds.[11]
(22) S. W. Benson, F. R. Cruikshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, **68**, 279 (1968).
(23) E. J. Hamilton and H. Fisher, *Helv. Chim. Acta*, **56**, 795 (1973).
(24) Kurt W. Egger and Alan T. Cocks, *Helv. Chim. Acta*, **56**, 1516 (1973).
(25) For a discussion of the error limits with this method, see ref 14.

expected, this value is lower than the 6.9-kcal/mol value for the rearrangement of cyclopropylmethyl to the 3-butenyl radical.[26] We can now apply a similar analysis to the 1-indanylmethyl to 2-tetralyl rearrangement, for which $\Delta H°_{298}$ =6.7 kcal/mol. Assuming a 3-kcal/mol well, we expect the forward 1,2 aryl migration to proceed with E_a = 16 kcal/mol and the reverse reaction to exhibit an activation barrier of 21.7 kcal/mol. With that figure of 22 kcal/mol, about one reverse rearrangement (2 to 1, eq 9)



(9)

1 10 2

would be observed for each 100 hydrogen abstractions by 2,[27] and thus the buildup of 1-methylindan via the reverse neophyl-like rearrangement is expected in high-temperature liquid-phase reactions, as is the case.[2,5,6] Ingold[28] reports that substitution of naphthyl or pyridyl for phenyl accelerates the forward 1,2 aryl migration rate by factors of ca. 50, corresponding to a factor of 5 at 427 °C. Thus, phenanthrene-substituted systems should exhibit reverse 1,2 aryl migration rates comparable to hydrogen abstraction rates in the liquid phase. In the gas phase, at radical and molecule concentrations of ca. 10^{-7} M as in this study, the conversion of 2 to 1 will be fast relative to radical–radical and radical–molecule reaction rates. Thus the observation of an apparently rapid equilibration of 1 and 2 at all temperatures is consistent with predicted thermochemical properties.

β-Scission/Recyclization Reactions. Scheme I depicts the principal pathways of interconversion of the indanylmethyl and tetralyl radicals. In Table VIII are listed estimated values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for these reactions. In the FVP experiments with precursors to 1 and 2, substantial yields of products derived from 1-tetralyl were observed (1,1′-bitetralyl, 1-methyltetralin). In the FVP experiment using the 1-tetralyl precursor, no indanylmethyl products are detected at 427 °C. An equilibrium mixture formed by the β scission of 1, recyclization to 4, and the reverse reaction would consist of 97% 1-tetralyl and 3% 1-indanylmethyl at 427 °C, from $\Delta G°$ = −4.77 kcal/mol. Thus, it appears that equilibration of 1-tetralyl and 1-indanylmethyl at 427 °C is not competitive with product-forming reactions. Two factors are responsible for these results: (1) the β scission of 4 to give 2-(*o*-vinylphenyl)ethyl (11) is expected to occur with an activation barrier of greater than 40 kcal/mol (see below), and (2) the recyclization of 11 to 4 is probably kinetically favored over closure to 1 (see below). The observation of 25% β-scission products from the FVP of the perester precursor of 2-methyl-1-indanyl, which should exhibit a similar activation barrier (see below), indicates that some β scission of 1-tetralyl is expected to occur, and the failure to trap a detectable yield of 1-indanylmethyl radicals at 427 °C further supports the view that recyclization of 11 to 4 is kinetically favored.

β scission of simple open-chain alkyl radicals occurs with Arrhenius activation barriers of 27–34 kcal/mol and *A* factors of $10^{14\pm0.5}$.[9] Examples include the β scission of *n*-butyl to ethyl and ethylene (E_a = 29 kcal/mol) and *sec*-butyl to propene and methyl (E_a = 34 kcal/mol).[29] The vast majority of addition reactions of simple hydrocarbon alkyl radicals to olefins occurs with E_a = 7 ± 2 kcal/mol and $A = 10^{8\pm0.5}$.[30,31] Little data on intramolecular cyclization rates exist. However, for the 5-hexenyl radical a "normal" E_a of 7.8 kcal/mol and log *A* = 10.7 have been determined for the kinetically controlled closure to cyclopentylmethyl.[32] However, steric inhibition of resonance or of proper approach to the olefin can be expected to substantially increase the E_a values.[17,31,33] In particular, cyclization of 11 to 1 can attain proper approach of the alkyl radical only if the π orbitals of the olefin are orthogonal to the π system of the aromatic ring. Thus, the E_a value for addition of ethyl to ethylene (6.9 kcal/mol)[30] is probably a good model for the cyclization of 11 to 1, since the rate enhancement of alkyl addition to styrene over ethylene[34] will be lost due to steric inhibition of resonance. To the value of 6.9 kcal/mol must be added 2.0 kcal/mol[35] for loss of resonance energy on rotation of the vinyl group to the orthogonal position. The resulting value of E_a = 8.9 kcal/mol is undoubtedly conservative, since $\Delta H°$(11 → 1) = 14.1 kcal/mol (Table VIII) implies an E_a for β scission of only 23 kcal/mol. A more realistic minimum barrier for the β scission, 29 kcal/mol, would necessitate a barrier for cyclization of 15 kcal/mol. By contrast, cyclization of 11 to 4 occurs with little deviation from the optimal approach to the olefin and only slight loss of resonance energy due to vinyl rotation. Thus, a "normal" activation barrier for cyclization of 5 kcal/mol[34] is expected. This neglects a small distortion of the vinyl double bond which may be necessary to achieve the transition state for cyclization. Since $\Delta H°$(11 → 4) = −34 kcal/mol, the β scission of 1-tetralyl is predicted to exhibit an E_a of 39–41 kcal/mol. Thus, cyclization of 11 to 4 is probably kinetically as well as thermodynamically favored over closure of 11 to 1. However, the difference in estimated E_a's is within the error limits of estimations of this type[11] and must await competitive kinetic studies of the cyclization of 11.

In directly analogous fashion, cyclization of *o*-allylbenzyl (12) to 2-indanylmethyl (3) requires complete localization of the benzyl radical to achieve the optimum geometry for closure.[19,33] The barrier for 90° rotation of the benzylic methylene, 13 kcal/mol,[36] must be added to the "normal" value of 7 ± 2 kcal/mol for an estimated value of 20 ± 2 kcal/mol from cyclization of 12 to 3. The value of $\Delta H°$(12 → 3) = −4.46 kcal/mol leads to an E_a for β scission (3 to 12) of 24.5 ± 2 kcal/mol. This value, which is several kilocalories per mole less than normal open-chain alkyl β scissions, suggests that E_a for cyclization of 12 to 3 is conservative at 20 kcal/mol. By contrast, cyclization of

(26) B. Maillard, D. Forrest, and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 7024 (1976).

(27) This assumes log *A* = 11.7 and E_a = 22000 for rearrangement, log *A* = 8.1 and E_a = 8000 for abstraction, and a 19.7 M abstractable hydrogen atom concentration at 427 °C (density of tetralin at 400 °C is 0.648 g/mL).[2] For data on tetralin and other alkyl radical abstraction rates, see Keith U. Ingold, "Free Radicals", Vol. I, Jay K. Kochi, Ed., Wiley-Interscience, New York, 1973, pp 37–112.

(28) K. U. Ingold, *ACS Symp. Ser.*, **No. 69**, 187–223 (1978).

(29) Sidney W. Benson and H. Edward O'Neal, *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.)*, **NSRDS-NBS-21** (1970).

(30) J. Alistair Kerr in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley-Interscience, New York, 1973.

(31) John M. Tedder and John C. Walton in "Advances in Physical Organic Chemistry", Vol. 16, V. Gold and D. Bethell, Eds., Academic Press, New York, 1978.

(32) D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).

(33) Reference 11, p 91; H. E. Gunning and R. L. Stock, *Can. J. Chem.*, **42**, 357 (1964); A. S. Gordon, *ibid.*, **43**, 570 (1965).

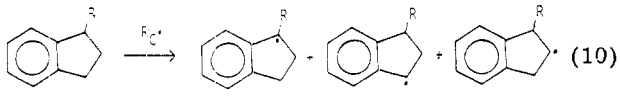
(34) A. Citterio, A. Arnoldi, and F. Minisci, *J. Org. Chem.*, **44**, 2674 (1979); L. S. Marcoux, R. N. Adams, and S. W. Feldberg, *J. Phys. Chem.*, **73**, 2611 (1969); R. F. Nelson and S. W. Feldberg, *ibid.*, **73**, 2623 (1969).

(35) Ted Schaefer and William J. E. Parr, *J. Mol. Spectrosc.*, **61**, 479 (1976).

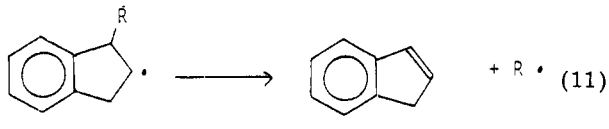
(36) Mark S. Conradi, Henry Zeldes, and Ralph Livingston, *J. Phys. Chem.*, **83**, 2160 (1979).

12 to 2 involves little steric inhibition of resonance in achieving the optimum approach of the alkyl radical to the olefin. Rates of addition of benzylic radicals to nonconjugated olefins are not available, although propagation rates for styrene polymerization show "normal" A factors (log A = 6.7 and 7.0, and E_a = 7.3 and 7.8).[34] Rates for β scission of benzylic radicals from simple aralkyl radicals are not available but are not expected to exhibit abnormal A factors and activation barriers. Thus, cyclization of 12 to 2 will certainly occur with an activation barrier of 7–10 kcal/mol, substantially below that of the cyclization of 12 to 3. Thus, a conservative estimate of activation barriers clearly points to both a kinetic and thermodynamic preference for closure of 12 to 2 over 3. The very small yields of 2-methylindan observed during the FVP of perester precursors of 1 and 2 at 427 °C are consistent with this view.

The detection of indene from the FVP experiments with the tetralyl and indanylmethyl precursors led us to examine the β scission reactions of 1-methyl-2-indanyl (6) and 2-methyl-1-indanyl (5) radicals. Under conditions of dissolution of coal at 427 °C, selectivities for abstraction of benzylic vs. secondary hydrogen by secondary alkyl radicals are expected to be about 6:1 or less.[27] Thus, 1-alkylindan and homologous systems are expected to undergo radical abstraction at the 2-position as well as the 1-position (eq 10). β scission of 1-alkyl-2-indanyl radical


(10)

(eq 11) will lead to dealkylation of isomerized tetralin or analogous reactions in tetrahydrophenanthrene systems.


(11)

The β scission of methyl from 6 occurs efficiently even at 327 °C. Using the β scission of the *sec*-butyl radical (E_a = 34 kcal/mol) as a model, we expect the β scission of 6 to be stabilized in the productlike transition state[20] by 2 kcal/mol of resonance energy[35] of the olefin due to conjugation with the aromatic ring. Thus, we expect an E_a for β scission of 32 ± 2 kcal/mol. Since $\Delta H°_{298}$ is 24 kcal/mol for the β scission, this value predicts an E_a = 8 ± 2 kcal/mol barrier for methyl addition to the 1-position of indene.

For the β scission of 2-methyl-1-indanyl to give indene and methyl, $\Delta H°_{298}$ = 37.5 kcal/mol. Addition of methyl radical to the 2-position of indene should show a rate enhancement over addition to a nonconjugated ethylene as in the case of addition of methyl to styrene.[34] Thus, E_a for addition of methyl could be as low as 5 kcal/mol, leading to an E_a for β scission of 42.5 ± 2 kcal/mol. The estimated values of 32 ± 2 kcal/mol for β scission of 6 and 42.5 ± 2 kcal/mol for 5 provide an approximate guide to the unimolecular rates achieved at 10^{-2} torr in the FVP reactor used in this study. The 25% yield of indene from 5 at 427 °C indicates that activation barriers of 43 kcal/mol are achievable in the FVP system at 427 °C and 10^{-2} torr. The yield of indene from β scission of 5 shows a much higher temperature dependence than that for 6, consistent with its expected higher activation barrier.

Conclusions

The results of this study show that several radical pathways for the rearrangement and fragmentation of tetralin, methylindans, and related hydroaromatic species are operable at elevated temperatures provided radical initiation processes occur. The interconversion of 1 and 2 occurs readily via a reversible 1,2 aryl migration. Thermochemical estimates of $\Delta H_f°$ of the neophyl-like rearrangement intermediates lead to an estimate of the barrier to ring opening of 8 of ca. 2 kcal/mol and hence to an E_a of only 22 kcal/mol for the reverse neophyl-like rearrangement of 2. Rearrangement of 4 to 2 is hampered by the apparently kinetically disfavored recyclization of 11 to 1 and the high activation barrier for the β scission of 4. These results indicate that the radical-induced isomerization of tetralin to methylindan is favored to proceed by the reverse 1,2 aryl migration of 2-tetralyl to 1-indanylmethyl. β scission reactions involving β-arylalkyl radicals may have activation barriers which are significantly lower than activation barriers for simple alkyl radicals due to benzylic resonance stabilization in the transition state. Thus radical-induced chain decomposition of the alkyl structure via β scission reactions can be expected to occur to at least a minor extent during coal dissolution in hydrogen-donor media, and this will depend in a complex fashion on the rate of generation of abstracting radicals and on the decomposition chain lengths during coal dissolution.

Experimental Section

General Procedures. ^{13}C and ^1H NMR spectra were determined with a Varian FT-80 FT NMR system operating at 20.000 or 79.54 MHz. Chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were determined by using a Perkin-Elmer Model 283 infrared spectrometer. Elemental analyses were determined for new compounds by Schwarzkopf Microanalytical Laboratories. Gas chromatography–mass spectrometry studies were conducted with a Hewlett-Packard Model 5982 instrument using 60-m SP-2250 and/or OV-101 glass-wall-coated open tubular capillary columns purchased from Scientific Glass Engineering, Inc. Analytical gas chromatography was conducted with the above columns and a Hewlett-Packard Model 5830A instrument equipped with flame-ionization detection.

Reagents. Peresters were synthesized by the method of Bartlett and Hiatt[37] and purified by preparative high-pressure liquid chromatography (LC) using a Waters Porasil B semipreparative column and a 1% solution of tetrahydrofuran (THF) in hexane as the mobile phase. The identity and purity of the peresters (95–99%) were established by NMR and IR spectroscopy, by analytical high-pressure LC (μ-Porasil, 1% THF in hexane), and in some cases by elemental analysis. Elemental analyses were not used in all cases since high-pressure LC monitoring of the purity of the peresters revealed that elemental analysis failed to reveal substantial percentages of decomposition products. ***tert*-Butyl tetralin-1-percarboxylate**: NMR ($CDCl_3$) δ 1.3 (s, 9 H), 1.9 (m, 4 H), 2.8 (t, 2 H), 3.9 (t, 1 H), 7.2 (s, 4 H). ***tert*-Butyl tetralin-2-percarboxylate**: NMR ($CDCl_3$) δ 1.3 (s, 9 H), 2.2 (m, 2 H), 2.9 (m, 5 H), 7.2 (s, 4 H). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.54; H, 8.12; O, 19.34. Found: C, 72.75; H, 7.78; O, 19.48. ***tert*-Butyl 1-indanperacetate**: NMR ($CDCl_3$) δ 1.3 (s, 9 H), 2.6 (m, 7 H), 3.6 (quintet, 1 H), 7.2 (s, 4 H). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.54; H, 8.12; O, 19.34. Found: C, 72.83; H, 7.85; O, 19.09. ***tert*-Butyl 2-indanperacetate**: ($CDCl_3$) δ 1.3 (s, 9 H), 2.9 (m, 7 H), 7.2 (s, 4 H). ***tert*-Butyl 1-methylindan-2-percarboxylate**: NMR ($CDCl_3$) δ 1.2 (d, 3 H), 1.3 (s, 9 H), 3.3 (m, 4 H), 7.2 (s, 4 H). ***tert*-Butyl 2-methylindan-1-percarboxylate**: NMR ($CDCl_3$) δ 1.2 (d, 3 H), 1.3 (s, 9 H), 2.6 (m, 3 H), 4.0 (m, 1 H), 7.2 (s, 4 H). The carbonyl regions of the IR spectra of all of the peresters were similar and exhibited a carbonyl band at 1765 cm^{-1}. Purity was checked before use by IR and high-pressure LC, and purification was repeated when decomposition products were detected. Tetralin-1- and -2-carboxylic

(37) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, 80, 1398 (1958).

acids were synthesized by Li/NH_3 reduction of 1- or 2-naphthoic acid (Aldrich) or purchased from Aldrich Chemical Co. 1- and 2-indanacetic acids were synthesized by the method described by Anderson and Wade.[38] 1-Methylindan-2-carboxylic acid was synthesized by catalytic hydrogenation of 1-methylindene-2-carboxylic acid (Aldrich) by using 10% Pd on carbon catalyst (Aldrich) at 70 psi of H_2 pressure in 85% ethanol. 2-Methylindan-1-carboxylic acid was synthesized from 2-indanone by steps involving reaction with methylmagnesium bromide, dehydration to 2-methylindene, carboxylation of lithium 2-methylindenylate, and catalytic hydrogenation.

Standards were purchased from chemical suppliers or synthesized by standard synthetic methods and their identities established by NMR, GC, GC–MS, and mass spectrometry. **1-Methylindan**: catalytic hydrogenation of 3-methylindene (Pfaltz and Bauer); NMR ($CDCl_3$) δ 1.3 (d, 3 H), 1.6 (m, 1 H), 2.3 (m, 1 H), 2.8 (m, 2 H), 3.2 (q, 1 H), 7.2 (s, 4 H). **1-Methylindene**: treatment of indene (Aldrich) with *n*-butyllithium and alkylation with methyl iodide; NMR ($CDCl_3$) δ 1.3 (d, 3 H), 3.5 (q, 1 H), 4.3 (dd, 1 H), 4.6 (dd, 1 H), 7.2 (m, 4 H). **2-Methylindene**: (1) reaction of methylmagnesium bromide and 2-indanone, (2) dehydration by refluxing in benzene with *p*-toluenesulfonic acid and 2 drops trifluoromethanesulfonic acid (similar conditions for dehydration were used for the compounds below); NMR ($CDCl_3$) δ 2.1 (s, 3 H), 3.3 (s, 2 H), 6.5 (s, 1 H), 7.2 (m, 4 H). **2-Methylindan**: catalytic hydrogenation of 2-methylindene (10% Pd/C, 70 psi of H_2, similar conditions for following compounds); NMR ($CDCl_3$) δ 1.2 (d, 3 H), 2.7 (m, 5 H), 7.2 (s, 4 H). ***cis*- and *trans*-1,3-dimethylindan**: (1) treatment of 3-methylindene with *n*-butyllithium and alkylation with methyl iodide, (2) catalytic hydrogenation, which formed the cis and trans isomers in 65% and 35% yields (1,1-dimethylindan was formed only in trace yields by this procedure); mixture ^1H NMR ($CDCl_3$) δ 1.28 (d, 6 H), 2.2–2.7 (m, 2 H), 3.4–2.8 (m, 2 H), 7.16 (s, 4 H). ***cis*- and *trans*-1,2-dimethylindan**: (1) alkylation of 2-methylindene with *n*-butyllithium and methyl iodide, (2) catalytic hydrogenation, which gave mostly one isomer (87.4%) by GC; ^1H NMR ($CDCl_3$) δ 1.0 (d, 3 H), 1.1 (m, 3 H), 2.9 (m, 4 H), 7.2 (s, 4 H). **1-Ethylindan**: (1) alkylation of indene with *n*-butyllithium and ethyl iodide, (2) catalytic hydrogenation; ^1H NMR ($CDCl_3$) δ 1.0 (t, 3 H), 1.7 (m, 2 H), 2.2 (m, 1 H), 2.8 (m, 4 H), 7.2 (s, 4 H). **2-Ethylindan**: (1) reaction of 2-indanone and ethylmagnesium iodide, (2) dehydration, (3) catalytic hydrogenation; ^1H NMR ($CDCl_3$) δ 1.0 (t, 3 H), 1.4 (m, 2 H), 2.8 (m, 5 H), 7.2 (s, 4 H). **1-Methyleneindan**: Wittig reaction of 1-indanone; ^1H NMR ($CDCl_3$) δ 2.8 (m, 4 H), 5.0 (t, 1 H), 5.5 (t, 1 H), 7.2 (m, 3 H), 7.5 (m, 1 H). **1-Methyltetralin**: Wolff–Kishner reduction of 4-methyl-1-tetralone (Aldrich); ^1H NMR ($CDCl_3$) δ 1.2 (d, 3 H), 1.8 (m, 4 H), 2.8 (t, 2 H), 3.0 (q, 1 H), 7.2 (m, 4 H). **2-Methyltetralin**: (1) reaction of β-tetralone and methylmagnesium bromide, (2) dehydration, (3) catalytic hydrogenation; ^1H NMR ($CDCl_3$) δ 1.1 (d, 3 H), 1.8 (m, 3 H), 2.8 (m, 3 H), 7.1 (s, 4 H). **1-*tert*-Butoxytetralin**: recovered from liquid-phase decomposition (25 °C, 2 weeks, neat) of *tert*-butyl tetralin-1-percarboxylate by preparative high-pressure LC and by preparative GC; ^1H NMR ($CDCl_3$) δ 1.4 (s, 9 H), 2.0 (m, 4 H), 2.8 (t, 2 H), 4.6 (t, 1 H), 7.2 (m, 3 H), 7.4 (m, 1 H); mass spectrum, *m/e* (relative intensity) no M^+, 130 (100), 131 (70), 120 (43), 57 (41), 147 (26). **2-Methyl-1-*tert*-butoxyindan**: prepared in same manner as for 1-*tert*-butoxytetralin; ^1H NMR ($CDCl_3$) 1.0 (d, 3 H), 1.1 (s, 9 H), 2.2–2.8 (m, 3 H), 4.8 (d, 1 H), 7.2 (m, 3 H), 7.4 (m, 1 H). **Methyl tetralin-1-carboxylate**: esterification of the acid in refluxing methanol over Linde 3-Å molecular sieves; ^1H NMR ($CDCl_3$) δ 1.9 (m, 4 H), 2.8 (t, 2 H), 3.8 (t, 1 H), 3.9 (s, 3 H), 7.2 (s, 4 H).

1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-binaphthyl (1,1′-Bitetralyl). This was prepared from 1-tetralol according to McMurray's procedure for coupling benzylic and allylic alcohols.[39] The pentane-soluble crude reaction mixture gave (GC) 17% tetralin, 18% 1,2-dihydronaphthalene, and 32% and 30% yields of *meso*- and *d,l*-1,1′-bitetralyl. The crude reaction mixture was passed through a short silica gel column (pentane) and then through a series of one 1000-Å, two 500-Å, and one 100-Å Waters Associates μStyragel gel-permeation columns (tetrahydrofuran eluent) to isolate the bitetralyls from tetralin and dihydronaphthalene. For the mixture: ^{13}C NMR ($CDCl_3$) δ 139.95, 139.17, 138.87, 138.54 (8a- and 8b-carbons, two for the meso and two for the *d,l* compound), 129.10 (two partially resolved peaks, 5-carbons of meso- and *d,l*), 128.42, 127.71 (8-carbon of meso and *d,l*), 125.76, 125.62, 125.37, 125.32 (6- and 7-carbons, two for meso and two for *d,l*), 43.19, 41.73 (1-carbon of meso and *d,l*), 30.62, 30.40 (4-carbon of meso and *d,l*), 27.57, 24.44 (2-carbon of meso and *d,l*), 22.50, 22.43 (3-carbon of meso and *d,l*); ^1H NMR ($CDCl_3$) δ 7.5–7.0 (m, 4 H), 3.8–3.3 (m, 2 H), 2.8–2.5 (t, 4 H), 2.1–1.2 (m, 8 H). Crystallization from methanol gave 15 mg of one of the diastereomers (mp 63–64.5 °C): mass spectrum, *m/e* (relative intensity) 262 (M^+, 1.7), 261 (5.5), 147 (5.9), 146 (16.9), 132 (13.1), 131 (100), 130 (27.4), 129 (24.8), 128 (13.7). The mass spectrum of the mixture was identical with that of isolated diastereomer.

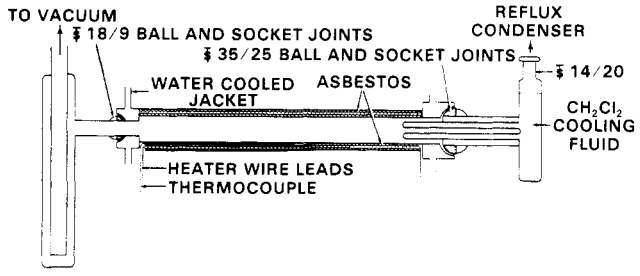


Figure 1. Flash vacuum pyrolysis (FVP) apparatus used in this study.

Flash vacuum pyrolysis (FVP) was carried out by evaporation of 15–30 mg of perester from a thermostated reservoir into a heated quartz reactor tube connected to a liquid nitrogen cooled trap attached to a high-vacuum system. A diagram of the apparatus appears in Figure 1. The reactor tube is 22 cm long and 2 cm in diameter with a 0.9 cm diameter exit aperature, corresponding to 220 wall collisions.[15] Water-cooled ball joints are used to connect the hot zone to the vacuum system. The temperature of the reactor tube is monitored by a thermocouple situated between the tube and the heating coils which are insulated with layers of asbestos. Temperature variations were maintained to ±5 °C. The reservoir containing the perester is thermostated by contacting its outer surfaces with methylene chloride (bp 40 °C), and it is so designed to deliver the vaporized perester molecules to the hot zone without contacting the water-cooled joints. Pressures between the cold trap and the exit of the tube were between 5×10^{-2} and 1×10^{-2} torr as measured with a Pyrani gauge. For the least stable peresters (1-tetralyl and 2-methyl-1-indanyl) the half-life of the neat perester was determined by control kinetic experiments to be ~4 h at 40 °C. The FVPs were all completed in less than 1 half-life. For a pyrolysis run, the apparatus was assembled with the perester in the reservoir, the reactor was brought up to a temperature (5–15 min), and then the cold trap was immersed in liquid nitrogen. The products were sampled for quantitative analysis by adding 3–5 mL of hexane and 3.0 μL (2.6 mg) of the internal standard *tert*-butylbenzene to the warmed trap and transferring the solution to a vial with a syringe equipped with a flexible Teflon tube. The cold trap contents of the lower temperature runs were analyzed by high-pressure LC which revealed complete decomposition of the peresters during FVP.

Analyses of Products. Product yields and distributions were obtained from GC analysis of samples by digital integration of peak areas, assuming a relative response factor to *tert*-butylbenzene of 1.0 for all compounds except 1,1′-bitetralyl and 2,2′-dimethyl-1,1′-biindan for which relative response factors of 0.5 were assumed. Conversion yields ranged from 48% to 91%. Product distributions were very reproducible and independent of conversion yields. The variation in the conversion yields was attributed to experimental errors associated with recovery of the small quantities of products formed. Conversion yields invariably improved when larger quantities of peresters were pyrolyzed.

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Acknowledgment. We gratefully acknowledge helpful discussions with Professor Sidney W. Benson concerning thermochemical estimates for radicals and neophyl-like rearrangement intermediates and with Dr. Donald M. Schoengold for gas chromatographic–mass spectral analysis and assistance in setup and operation of a capillary GC system.

Registry No. 1, 75421-36-2; 2, 75421-37-3; 3, 75421-38-4; 4, 69339-77-1; 5, 75421-39-5; 6, 75421-40-8; 8, 75494-99-4; 9, 31987-29-8; 10, 75495-00-0; 11, 75421-41-9; 12, 75421-42-0; *tert*-butyl 1-methylindan-2-percarboxylate, 75421-43-1; *tert*-butyl 2-methylindan-1-percarboxylate, 75421-44-2; *tert*-butyl 1-indanperacetate, 75421-45-3; *tert*-butyl tetralin-2-percarboxylate, 75421-46-4; *tert*-butyl 2-indanperacetate, 75421-47-5; *tert*-butyl tetralin-1-percarboxylate, 75421-48-6; indene, 95-13-6; 1-methylindan, 767-58-8; 3-methylindene, 767-60-2; *cis*-1,2-dimethylindan, 39172-70-8; *trans*-1,2-dimethylindan, 70282-84-7; 1-methylindene, 767-59-9; methyl 1-methylindan-2-carboxylate, 75421-49-7; 1-methyl-2-*tert*-butoxyindan, 75421-50-0; 2-methylindan, 824-63-5; 2-methylindene, 2177-47-1; 2,2'-dimethyl-1,1'-biindan, 75421-51-1; *trans*-1-*tert*-butoxy-2-methylindan, 75421-52-2; methyl 2-methylindan-1-carboxylate, 75421-53-3; *cis*-1,3-dimethylindan, 26561-33-1; *trans*-1,3-dimethylindan, 40324-83-2; 1-methyleneindan, 1194-56-5; 2-methyleneindan, 68846-65-1; 1-ethylindan, 4830-99-3; tetralin, 119-64-2; 1,2-dihydronaphthalene, 447-53-0; 1,4-dihydronaphthalene, 612-17-9; 2-methyltetralin, 3877-19-8; 1-methyltetralin, 1559-81-5; naphthalene, 91-20-3; *meso*-1,1'-bitetralyl, 75421-54-4; *dl*-1,1'-bitetralyl, 75421-55-5; 2-ethylindan, 56147-63-8; 1-*tert*-butoxytetralin, 75421-56-6; methyl tetralin-1-carboxylate, 17502-86-2; *cis*-1-*tert*-butoxy-2-methylindan, 75421-57-7.

Conformation in Solution of Sterically Hindered Sulfoxide and Sulfone Alcohols

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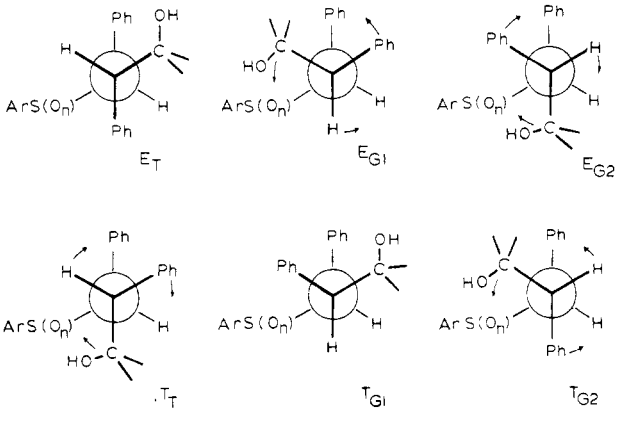
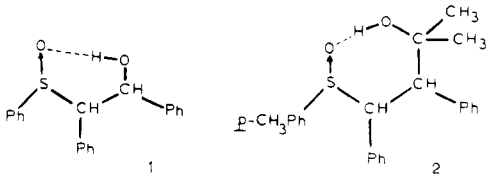
The conformations of the isomeric 2-methyl-3,4-diphenyl-4-(4-methylthiophenoxy)-2-butanols, 2-methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanols, and 2-methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanols have been studied by means of NMR and infrared spectroscopy. In contrast to the 2-(benzenesulfinyl)-1,2-diphenyl-1-ethanols of a previous study, three of the four isomeric alcohols showed evidence for intramolecular hydrogen bonding in solution, although a seven-membered ring results upon hydrogen bonding. However, in one isomer, the hydrogen bonding is weak. In another isomer, a strong hydrogen bond is present, although hydrogen-bond formation occurs at the expense of considerable deformation of the molecule from the usual type of structure having dihedral angles close to 60°. X-ray crystallographic data also show a tendency of this type of molecule to adopt a solid-state conformation having markedly variable dihedral angles.

Molecules having possibilities for intramolecular hydrogen bonding offer some of the most interesting problems in acyclic conformational analysis.[1] The question of interest concerns the extent to which intramolecular hydrogen bonding is able to overcome the repulsive interactions of large groups and force the population of otherwise disfavored conformers.

In these studies, the sulfoxide group is useful as a hydrogen-bond acceptor. Sulfoxides are among the strongest acceptors; in fact, addition of dimethyl sulfoxide to water results in the liberation of considerable heat.[2b] The sulfoxide also is chiral, and the effect of configuration at sulfur is of interest. In previous studies of sulfoxide alcohols (i.e., **1**),[3] internal hydrogen bonding prevailed in only

Scheme I





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