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Thermolysis of Model Compounds for Coal. 2. Condensation and Hydrogen Transfer during Thermolysis of Naphthols[1-3]

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The dominant initial products from thermolysis of 1-naphthol in the liquid phase at 400 °C are 2,2′-binaphthalene-1,1′-diol (**2**) and 1-tetralone (**6**). As reaction proceeds, binaphthol **2** undergoes rapid cyclization to dinaphtho[1,2-*b*:2′,1′-*d*]furan (**1**), while ketone **6** is more slowly converted ultimately to naphthalene (**8**). The initial rate of this ring coupling and hydrogen-transfer reaction shows an apparent kinetic order of ~2.5 in *m*-terphenyl diluent. In benzophenone solvent, formation of coupled binaphthol **2** is accelerated, but reduced product **6** is replaced by diphenylmethane. Thermolysis of 2-naphthol behaves similarly except that coupling occurs both between C-1 and C-1′ to give dinaphtho[2,1-*b*:1′,2′-*d*]furan (**3**), preceded by 1,1′-binaphthalene-2,2′-diol (**4**), and between C-1 and C-3′ to give dinaphtho[2,1-*b*:2′,3′-*d*]furan (**5**). The major reduction product is 2-tetralone (**14**). The ratio of (**3** + **4**)/**5** decreases with increasing reaction time. Mechanistic hypotheses for this characteristic thermal behavior of phenols are explored. The significance of the reactions involved for conversion processes for coal, which contains significant phenolic functionality, is discussed.

The desire to understand the organic chemistry underlying various potential processes for conversion of coal to synthetic fuels and/or feedstocks has generated renewed interest in the thermal chemistry of key structural features present in coal. One such feature is phenolic hydroxyl groups which constitute a significant fraction of the oxygen content of coals[4a,5] and coal-derived process solvents.[6] To interpret the phenomenology associated with coal liquefaction in hydrogen-donor solvents,[4b,c,7,8] for example, one would need to know the reaction pathways available to typical phenolic materials at 400–500 °C,[9] or, to understand flash pyrolysis,[4d] corresponding chemical information at 800–1000 °C would be very valuable. However, among the classes of organic compounds for which detailed thermolysis behavior is available,[13] phenols are notable by their infrequency of study. Hence, there is a need for thermolysis studies of typical phenols as a function of chemical structure, reaction conditions, and added reagents and catalysts.

After considering the relevance to presently envisioned coal structures,[4a,5a] the literature background on thermolysis of phenols, the results of preliminary scouting experiments, and certain factors of initial experimental convenience, we chose to begin such model compound studies with the isomeric naphthols under liquid-phase conditions at temperatures where reactions first appear at significant rates (~400 °C). This paper describes some chemistry occurring in this reaction regime and provides

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

[2] Paper 1: Poutsma, M. L. *Fuel* **1980**, *59*, 335.

[3] Preliminary results presented in the following: Poutsma, M. L.; Dyer, C. W. *Proc. Int. Conf. Coal Sci.* Düsseldorf, Verlag Glückauf, GmbH, Essen, 1981, p 669. Poutsma, M. L. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1980**, *25*(1), 30.

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[7] The effects of the phenolic content of process solvents on liquefaction performance have been reviewed recently by Larsen, J. W.; Sams, T. L.; Rodgers, B. R. *Fuel* **1981**, *60*, 335.

[8] (a) Whitehurst, D. D.; Mitchell, T. O.; Farcasiu, M. "Coal Liquefaction"; Academic Press: New York, 1980. (b) Berkowitz, N. "An Introduction to Coal Technology"; Academic Press: New York, 1979.

[9] Among recent suggestions for possible reactions of phenols during liquefaction are formation of diaryl ethers (ref 10), hydrogen donation to degrading coal (ref 10, 11), hydrogen-atom transport (ref 7), homolytic substitution by coal-derived radicals (ref 10), and promotion of homolysis of aryl ethers by hydrogen bonding (ref 12).

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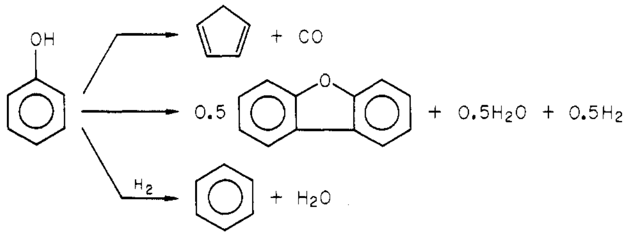
the background for subsequent, more detailed mechanistic considerations.

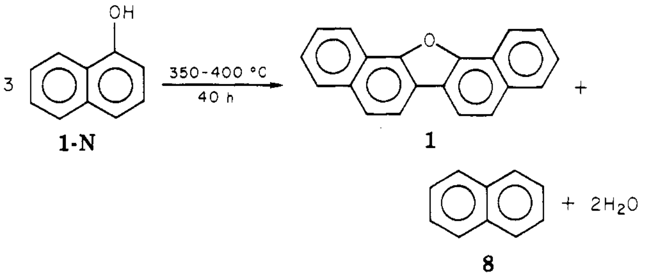
Historical Background

Information on thermolysis of phenol itself is limited, especially under conditions where there are no other added reagents or catalytic surfaces. Briner[14] reported that phenol was 50% consumed by heating at 450 °C in the gas phase at ~100 kPa pressure for 20 h; increasing the pressure to 500 kPa increased consumption to 96% after only 8 h. The products were assumed to be diphenyl ether and water, but this was not experimentally verified. Bahr[15] observed formation of both diphenyl ether and dibenzofuran in flow thermolysis of gaseous phenol diluted with nitrogen over activated charcoal at 300–500 °C. At 650 °C over a pumice packing, Hagemann[16] obtained a complex mixture of hydrocarbons, ranging from methane to polynuclear aromatics, along with carbon monoxide and hydrogen gases. In these latter two cases, a catalytic role for the solids cannot be ruled out.

The most detailed information has been obtained recently by Braekman-Danheux and Heyvaert[17] and by Cypres and Bettens[18] from gas-phase thermolysis of phenol in a nitrogen carrier at 665–865 °C and 2.5-s contact time. Some seven gaseous products, more than 50 liquid products ranging from cyclopentadiene to benzofluoranthene, and a solid carbonaceous residue were detected. For example, at 780 °C (14% conversion), the major products, in descending order of amount, were carbon monoxide, water, residue, hydrogen, benzene, naphthalene, methane, dibenzofuran, indane, and cyclopentadiene. On the basis of product analyses and results with radiolabeled phenol, Cypres and Bettens[18] proposed three distinct competitive processes which consume phenol: (1) *decarbonylation* to form carbon monoxide and cyclopentadiene, further thermolysis[19] of which then gives many of the hydrocarbon products; (2) *condensation* to form dibenzofuran, water, and hydrogen; and (3) *dehydroxylation* by hydrogen to form benzene and water. Clearly a very complex set of parallel and consecutive reactions with comparable rates must be involved in this temperature–pressure range. The relative dependencies of these three processes on reaction parameters were not elucidated, nor were detailed mechanisms unraveled. A still different product type, *p*-terphenyl, was claimed by Voronkov[20] from thermolysis at 750 °C in a recirculating flow system.



Literature on thermolysis of the naphthols suggested to us that product mixtures might be simpler than those from phenol and that at least some of the competitive processes might be separable on the basis of differing response to reaction temperature. Data under purely thermal conditions at <500 °C is largely limited to a single, 100-year old study by Merz and Weith.[21] From heating 1-naphthol (**1-N**) in a sealed tube at 350–400 °C for 40 h under largely liquid-phase conditions, they isolated three neutral products in modest yield: water, naphthalene, and a compound $C_{20}H_{12}O$. The acidic fraction of the crude product contained unidentified material less volatile than **1-N**. The lack of pressure buildup in the sealed tube suggested the absence of significant formation of hydrogen or carbon monoxide gases. Bis(1-naphthyl) ether was not detected. The same condensation–dehydration–dehydrogenation product $C_{20}H_{12}O$ has subsequently been formed by heating **1-N** at lower temperatures with a variety of oxidizing or dehydrogenating agents such as air,[21] lead oxide,[22] vanadium pentaoxide,[23] phosphorus,[24] selenium,[25] or benzophenone.[11] A definitive structural assignment as dinaphtho[1,2-*b*:2′,1′-*d*]furan (**1**) was ultimately made[26] on the basis of its synthesis from thermal cyclization of 2,2′-binaphthalene-1,1′-diol (**2**), the minor oxidative coupling product formed from **1-N** with ferric ion in aqueous solution.[27] Merz and Weith[21] assigned the following partial stoichiometry to the thermal reaction:



Since bis(1-naphthyl) ether was found to be thermally more stable than **1-N**, it was excluded as an intermediate by these workers.[21]

Analogous thermal decomposition of 2-naphthol (**2-N**) proceeded more slowly. The distinctive product was a second $C_{20}H_{12}O$ isomer which appeared to be identical with dinaphtho[2,1-*b*:1′,2′-*d*]furan (**3**) which could be prepared by cyclization[23,28–31] of 1,1′-binaphthalene-2,2′-diol (**4**), the major oxidative coupling product[23,28] of **2-N**. Much later, however, Clemo and Spence[23] heated **2-N** from 270 to 340 °C over a 10-h period while exposed to air in the presence of calcium oxide and isolated a dinaphthofuran which was different from the cyclization product of binaphthol **4**. On the basis of its oxidation to an isolable mono-*p*-quinone[32] under conditions where isomer **3** was destroyed, the new isomer was assigned the unsymmetrical structure dinaphtho[2,1-*b*:2′,3′-*d*]furan (**5**). Clemo and Spence[23] therefore concluded that the furan originally isolated by

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[15] Bahr, T. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2258.

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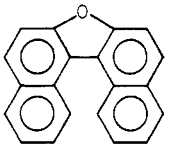
Table I. Thermolysis of Liquid-Phase 1-Naphthol at 400 °C[a]

time,[b] min	conver-sion, %	product distribution[d] (1-N equivalents[c]), %										
		1	**2**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	*e*	*f*
5	2.9[g]	33	27	24	4.0	0.8	0.5	1.2	<1.3	3.8	1.2	2.9
15	7.2[g]	46	15	24	4.5	0.9	0.9	1.5	<1.5	1.4	1.4	3.0
22.5[h]	12.1[g]	53	6	18	3.8	1.4	2.0	3.0	<2.1	1.6	<2.2	5.9
30	16.1[g]	47	16	26	3.5	1.2	1.2	2.5		0.1	1.2	2.6
30	18.8[g]	54	7	20	5.5	1.5	2.1	1.4	1.3	0.7	1.8	5.1
75[i]	32[g]	55	5	18	4.0	2.3	3.2	2.7	0.7	0.3	2.4	7.0
240	55,[g] 64[j]	63	3	12	3.1	4.6	4.9		0.8	0.3	2.9	6.0
960	66,[g] 83[j]	64	2	4.7	1.3	11.9	4.0[k]		0.8	0.6	4.0	5.4

[a] 4.8 ± 0.3 mmol of **1-N** in a 6.8 ± 0.2 mL tube. [b] Includes heatup time of ~1 min. [c] "1-N equivalents" for each product obtained by multiplying molar amount by (carbon number)/10 and hence represents relative amounts of **1-N** consumed. [d] **1** = dinaphtho[1,2-*b*:2',1'-*d*]furan; **2** = 2,2'-binaphthalene-1,1'-diol; **6** = 1-tetralone; **7** = 5,6,7,8-tetrahydro-1-naphthol; **8** = naphthalene; **9** = tetralin; **10** = 1-tetralol; **11** = bis(1-naphthyl) ether; **12** = 1,1'-binaphthalene-4,4'-diol. [e] Sum of two unidentified nonphenolic products. [f] Sum of two naphthylnaphthols. [g] Based on total observed products. [h] (H_2O)/(**1** + **8** + **9** + *e*) = 0.93. [i] <0.1% noncondensable gas. [j] Based on **1-N** recovered. [k] 1.3% indan plus 1-methylindan.

Merz and Weith[21] from the thermal reaction was, in fact, isomer **5**. Unfortunately, ambiguity remains because the experimental record does not indicate whether Clemo and Spence[23] ever reproduced the original conditions[21] in the *absence* of air and calcium oxide. In retrospect (see below), we can see that this confusion arose because dinaphthofuran isomers **3** and **5** have almost identical melting points and produce a set of mono- and dipicrates (and mixtures thereof), the interpretation of whose melting points has led to more confusion than clarification.[21,23,24,28-31] In any case, *condensation* to form dinaphthofurans and *dehydroxylation* to form naphthalene appear to be the dominant features of thermolysis of the naphthols in the condensed phase at ~400 °C.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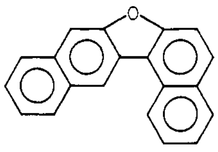
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In contrast, at much higher temperatures in the gas phase, *decarbonylation* appears to dominate. For example, flow thermolysis of either naphthol isomer at 900 °C and ~3 Pa gave indene as the characteristic organic product.[33]

At an intermediate temperature (660 °C) in flowing nitrogen gas, Hagemann[16] found gaseous products consisting of both carbon monoxide and hydrogen. From the complex mixture of condensable products, three superficially analogous materials were isolated in modest yield from each isomeric naphthol. **1-N** gave naphthalene (~5%), dinaphthofuran **1** (~14%), and an unidentified hydrocarbon (~5%), suggested to be $C_{22}H_{30}$. **2-N** gave naphthalene (~6%), an O-containing product (~13%) having an analysis and melting point not grossly inconsistent with dinaphthofuran **3** or **5** (although the author proposed a dinaphthopyran structure), and a hydrocarbon (~10%), proposed to be 1,2-bis(2-naphthyl)ethylene. Thus in this intermediate temperature range there is again some evidence, as for phenol, of competitive *condensation*, *dehydroxylation*, and *decarbonylation*. At 700 °C in flowing steam, Russian workers[34] more recently reported formation of hydrogen, carbon monoxide, naphthalene, and indene from **1-N** and of carbon monoxide, hydrogen, and indene from **2-N**. The authors[35] of another gas-phase study at 700–950 °C described the major pathways in terms of competition between decarbonylation and dehydroxylation which requires hydrogen from an unspecified source. Neither of these studies[34,35] describe the heavier products reported by Hagemann.[16]

Hall[36] examined the behavior of naphthols at 400–500 °C for 2 h under hydrogen pressure (~23 MPa). A major constituent of the neutral products from **1-N** at 400 °C was assigned as dinaphthofuran **1**. As temperature (and extent of conversion) increased, formation of naphthalene and tetralin increased, and 2,2'-binaphthalene gradually replaced product **1**. From **2-N** at 400 °C were found a dinaphthofuran (**3** or **5**, ?) and bis(2-naphthyl) ether. Again higher temperatures promoted formation of naphthalene, tetralin, and, in this case, 1,1'-binaphthalene. Hall[36] proposed that furan formation was preceded by ether formation. Control experiments in the absence of hydrogen were not reported.

Raaen and Roark[11] heated **1-N** at 400 °C for 17 h in the presence of excess benzophenone and isolated dinaphthofuran **1** in 80% yield. This yield exceeds the stoichiometry proposed by Merz and Weith[21] for the thermal reaction, and indeed a reduction product of benzophenone, i.e., diphenylmethane, was formed as a coproduct.

Results

1-Naphthol. Purified 1-naphthol (**1-N**) was heated in individual degassed sealed Pyrex tubes at 400 °C for periods ranging from 5 min to 16 h. The amount of **1-N** normally used relative to the tube volume was such that it was distributed in a 3:1 ratio between a liquid phase and a vapor phase at a vapor pressure of ~950 kPa.[37] At low conversions, only a barely detectable yellow color developed and, even to the highest conversions studied (~80%), the brown product mixture was completely soluble in benzene. Product analyses by GC were carried out on the reaction mixtures as produced, after extraction with aqueous base to remove unreacted **1-N** and phenolic products, and after trimethylsilylation. The latter procedure was necessary to obtain quantitative data for the less volatile phenolic products. Product assignments were made from GC–MS data compared with those of authentic materials (see Experimental Section).

At the lowest conversion studied (2.9%, 5 min), the dominant products were the condensed dinaphthofuran **1** (33%; see Table I, footnote *c* for conventions regarding

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(33) Schaden, G. *Justus Liebigs Ann. Chem.* **1978**, 559.

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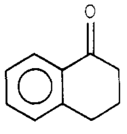
(36) Hall, C. C. *Fuel* **1933**, *12*, 419.

(37) "CRC Handbook of Chemistry and Physics"; 58th ed.; Chemical Rubber Publishing Co.: Cleveland, 1977.

units), the structurally related binaphthol **2** (27%), and a formal reduction product, 1-tetralone (**6**) (24%). Minor products included 5,6,7,8-tetrahydro-1-naphthol (**7**; 4%), naphthalene (**8**; 0.8%), tetralin (**9**; 0.5%), 1-tetralol (**10**; 1.2%), bis(1-naphthyl) ether (**11**; ≲1.3%), 1,1′-binaphthalene-4,4′-diol (**12**; 3.8%), two naphthylnaphthols of unidentified positional isomerism (2.9%), and two nonphenolic products of retention time appropriate for C_{20} materials (1.2%). The distribution among the products changed significantly as reaction time and conversion level increased. A sharp increase in the relative amount of dinaphthofuran **1** was almost exactly mirrored by a decrease in binaphthol **2**. Secondly, ketone **6** was more gradually replaced by a mixture of naphthalene and tetralin. However, none of the other minor products ever increased in relative importance. Data are summarized in Table I for conversions ranging from 2.9% to >65%. At a conversion level of 55–65% where the amount of residual **1-N** could be accurately compared with the amount charged, these detected organic products accounted for 85% of the **1-N** consumed; the material balances at lower conversions are almost surely even higher. Water product could be easily detected, but no noncondensable gas (e.g., hydrogen) was found.



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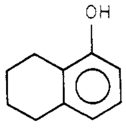

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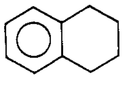

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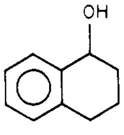

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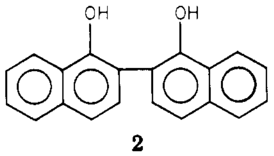

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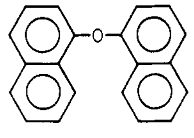

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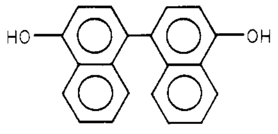

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The thermal behavior of some possible intermediates between **1-N** and dinaphthofuran **1** was compared in a series of parallel runs at 400 °C for 30 min, conditions sufficient to consume 16–19% of **1-N** itself (Table I). Ether **11** (0.21 mmol in a 6.9-mL tube) gave no detectable products. In contrast, binaphthol **2** (0.19 mmol in a 6.5-mL tube) was >99% consumed to give largely dinaphthofuran **1** but also some **1-N** (molar ratio = 2.6:1.0). Binaphthol **12** (0.23 mmol in a 6.7-mL tube) was comparably reactive to **1-N** (21% consumed); the only significant product observed by GC analysis was **1-N** in a selectivity of ~30%.

Thermolysis of **1-N** in the gas phase gave very similar products but at a much slower rate. In contrast to liquid-phase behavior, quantitative reproducibility from run to run was rather poor. Because of this behavior, which probably results from uncontrolled wall effects, we refrain from listing extensive results here. The range of variability is typified by the following selected extreme results obtained at 400 ± 50 kPa. Two particular runs each achieved 5% conversion and, in each case, the major products were dinaphthofuran **1** and ketone **6** in an equivalent ratio of 2.5 ± 0.1:1.0; these product results are thus consistent with liquid-phase data. Yet the times necessary to achieve this conversion were, in one case, 16 h and, in the second, 64 h. In spite of this variability, if one notes that 5% conversion in the liquid phase was achieved in only ~0.15 h (Table I), we can conclude that for the "liquid-phase" behavior emphasized herein, the ~25% of **1-N** in the gas phase should contribute a negligible amount to the overall reaction because of the much slower gas-phase rate.

Table II. Thermolysis of 1-Naphthol in *m*-Terphenyl at 400 °C

charge,[a] mmol		time,[b] min	condensed products **1** and **2**	
1-N	*m*-terphenyl		(1-N mequiv)	conversion, %
4.74	0	22.5	0.34	7.2
4.90	1.50	30	0.31	6.3
1.21	3.98	120	0.044	3.6
0.94	4.26	420	0.077	8.2
0.46	3.97	1440	0.078	17.0

[a] Tube volume 6.8 ± 0.2 mL. [b] Includes heatup time of ~1 min, which was subtracted in calculating rates shown in Figure 1.

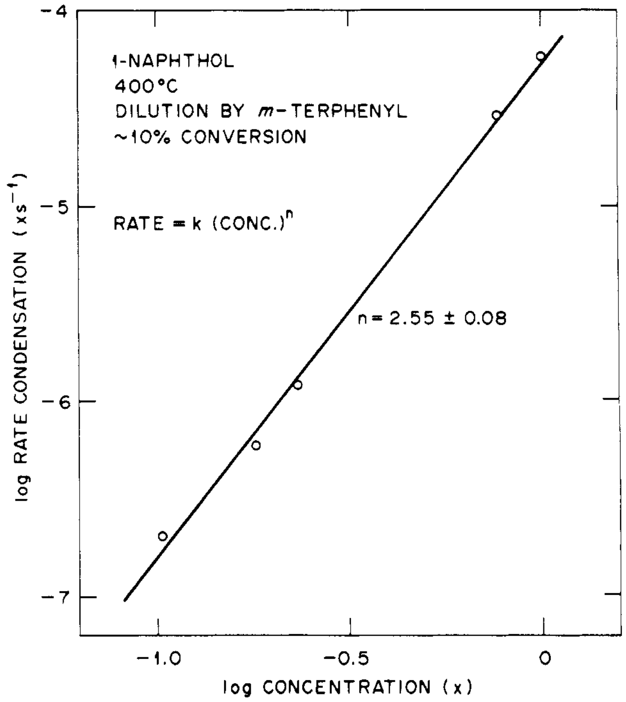

Figure 1. Initial rates of condensation of **1-N** as a function of dilution by *m*-terphenyl; see Table II.

For exploration of the effects of an inert diluent on the initial liquid-phase thermolysis rate, a series of low-conversion runs was performed in *m*-terphenyl (estimated vapor pressure at 400 °C is 200–225 kPa) as solvent. At 400 °C for the reaction times employed, *m*-terphenyl alone gave no significant detectable products, and there were no unexpected extra products in the mixed runs with **1-N**. Results are shown in Table II where the combined total of the condensed products **1** and **2** (60–65% of the total reaction) is used as the indicator of the extent of reaction. Initial rates of condensation were then approximated from these "one-point", low-conversion runs and were expressed in units of mol fraction (x)/unit time.[38] A log–log plot of these data is shown in Figure 1 with a linear least-squares fit.

Dilution with *m*-terphenyl gave no major changes in product patterns. In contrast, dilution with benzo-

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[38] Lack of experimental density values for reaction mixtures at 400 °C precluded conversion to customary molarity units.

Table III. Thermolysis of Liquid-Phase 2-Naphthol at 400 °C[a]

time,[b] min	conversion,[c] %	product distribution (2-N equivalents),[d,e] %							$\mathbf{13}^{e,f}$ / Σ other products
		3	**4**	**5**	**16**[g]	**14**	**15**	**8**	
10	1.1	1.0	54	17	3.1	23	1.0	0.8	0.32
20	0.8	2.2	52	18	2.7	20	2.9	1.0	0.89
40	2.6	3.2	48	24	1.3	20	2.3	0.8	0.13
60	3.4	6.4	42	26	0.9	19	4.2	1.2	0.47
180	5.2	16	28	30	0.6	15	6.2	2.4	0.67
275	7.5	23	21	37	0.4	12	2.4	3.8	0.72
420	10.6	13	10	49	0.8	19	4.0	3.8	0.16
975	17	34	2.0	40	1.5	11	6.1	4.8	0.81
2410	26	18	1.3	56	1.3	8	1.9	14	0.10

[a] 4.6 ± 0.2 mmol of **2-N** in a 6.8 ± 0.2 mL tube. [b] Includes heatup time of ~1 min. [c] Based on total observed products excluding **13**. [d] See footnote *c*, Table I. [e] **3** = dinaphtho[2,1-*b*:1′,2′-*d*)furan; **4** = 1,1′-binaphthalene-2,2′-diol; **5** = dinaphtho[2,1-*b*:2′,3′-*d*]furan; **13** = bis(2-naphthyl) ether; **14** = 2-tetralone; **15** = 5,6,7,8-tetrahydro-2-naphthol; **16** = 1,3′-binaphthalene-2,2′-diol. [f] Equivalent units. [g] Tentative assignment.

phenone[11] led to an acceleration of formation of the condensed products **1** and **2**, but the normal reduced products, principally ketone **6**, were replaced by diphenylmethane. For example, thermolysis of a 78:22 molar ratio mixture of **1-N** and *m*-terphenyl at 400 °C for 30 min would be predicted to give 6% conversion to condensed products by interpolation within Figure 1. Such a mixture of **1-N** and benzophenone gave 26% conversion to condensed products (**2**/**1** = 0.32). However, the only other major product observed was diphenylmethane with (**1** + **2**)/Ph_2CH_2 = 2.05 (molar ratio).

2-Naphthol. Because of the literature confusion regarding the identities of dinaphthofurans **3** and **5** (see Historical Background), it was necessary to clarify this structural question first. Pure samples of the isomeric dinaphthofurans **1**, **3**, and **5** were obtained as indicated in the Experimental Section. ^{13}C NMR data (20 MHz) are shown schematically in Figure 2 compared with published data[39] for dibenzofuran as a model. The doubled number of lines in the lowest spectrum immediately associates it with isomer **5**, which lacks the C_{2v} symmetry of isomers **1** and **3**. The distinctive high-field line in dibenzofuran at 111.4 ppm, assigned[39] to the proton-bearing carbon β to oxygen (C_4), has its analogues in isomer **3** at 112.5 ppm and in isomer **5** at 107.0 and 112.4 ppm. The carbons β to oxygen in isomer **1** are all at ring junctions and hence occur at lower field. The distinctive low-field line for the carbon α to oxygen, which occurs at 156.1 ppm in dibenzofuran, is found in isomers **1**, **3**, and **5** at 151.5, 154.2, and (154.5, 156.0) ppm, respectively. Also listed in Figure 2 are the lowest field ^1H NMR lines (200 MHz), which are the most distinctive feature of the ^1H NMR spectra. Isomer **1** from **1-N** has a broadened doublet at 8.79 ppm, which we assign to H-1 held rigidly in the peri position relative to oxygen; this structural feature gives the lowest field proton resonance in, for example, **1-N** itself[40a] and 1-methoxynaphthalene.[40b] The symmetrical isomer **3** from **2-N** has an even lower field doublet at 9.32 ppm; this we assign to H-1 in analogy to the deshielding effects experienced by overcrowded hydrogens in the helicenes.[41] In the unsymmetrical isomer **5** from **2-N**, nonequivalent H-1 and H-13 each experience the same phenomenon but to a lesser degree.

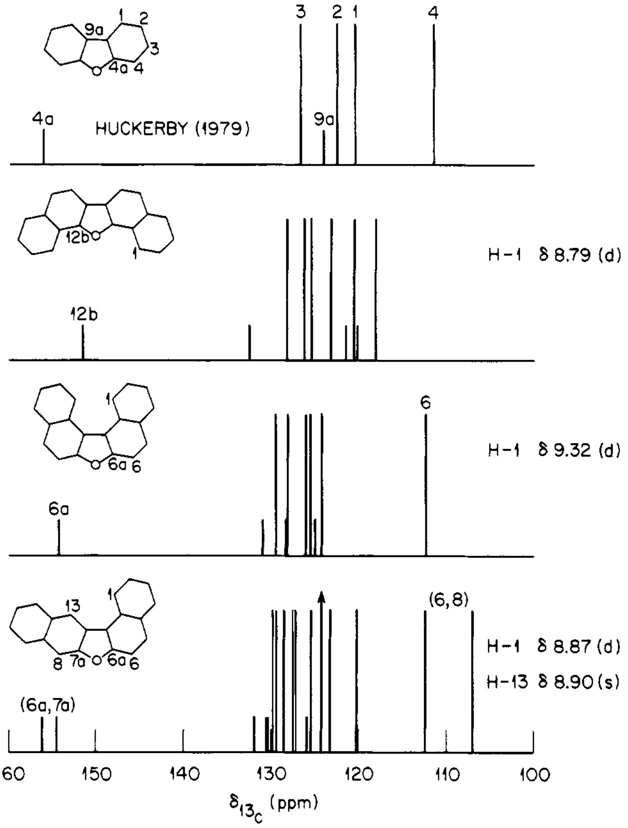

Figure 2. Schematic representation of ^{13}C NMR spectra of dibenzofuran and dinaphthofurans **1**, **3**, and **5**. Taller lines represent proton-bearing carbons and shorter lines represent non-proton-bearing carbons (ring fusions). Distinctive low-field lines in the ^1H NMR spectra are listed at the right side.

Thermolysis of **2-N** in the liquid phase at 400 °C proceeded somewhat more slowly than that of **1-N**. At low conversions, the products identified were symmetrical dinaphthofuran **3**, the structurally related binaphthol **4**, the unsymmetrical dinaphthofuran **5**, bis(2-naphthyl) ether (**13**), 2-tetralone (**14**), 5,6,7,8-tetrahydro-2-naphthol (**15**), and naphthalene (**8**). A minor product, detected only after trimethylsilylation, is suspected to be the binaphthol **16**, related to dinaphthofuran **5**, on the basis of its mass spectrum, but positive identification has not yet been achieved. No 2-tetralol could be detected. The distribution among these products as a function of reaction time is shown in Table III. Because the fraction of ether **13** formed varied much more widely and irregularly from run to run than did that of the other products, it has been tentatively assumed that it does not lie on the inherent thermolysis pathway but rather results from an adventitious, possibly wall-catalyzed reaction. On this basis, it

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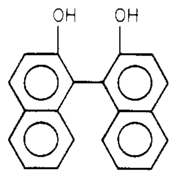
(39) Huckerby, T. N. *J. Mol. Struct.* **1979**, *54*, 95.

(40) Emsley, J. W.; Salman, S. R.; Storey, R. A. *J. Chem. Soc. B* **1970**, 1513. (b) Lucchini, V.; Wells, P. R. *Org. Magn. Reson.* **1976**, *8*, 137.

(41) Martin, R. H.; Defay, N.; Figeys, H. P.; Flammang-Barbieux, M.; Cosyn, J. P.; Gelbcke, M.; Schurter, J. J. *Tetrahedron* **1969**, *25*, 4985.



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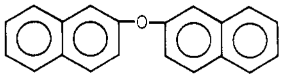

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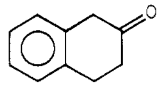

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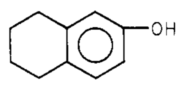

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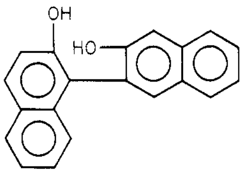

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is not included in the calculated conversion values listed in Table III; however, the amount of ether relative to all other products is shown separately.

The trends in product distribution with increasing conversion do not appear as smooth as they were for **1-N** because of more experimental scatter. Nevertheless, certain features are clear. Note first that *both* dinaphthofurans **3** and **5** were produced. The binaphthol/dinaphthofuran ratios for structurally related cases (**4**/**3** and **16**/**5**) decreased with increasing conversion as did the corresponding ratio **2**/**1** from **1-N**. At comparable low conversion levels (~3%), this value was the largest (~10) for the symmetrical condensation process from **2-N**, intermediate (~0.8) for the condensation process from **1-N**, and smallest (≲0.04) for the unsymmetrical condensation process from **2-N**. The relative amount of the sum of the symmetrical condensation products (**3** + **4**) gradually decreased, while that of the unsymmetrical analogues (**5** + **16**) correspondingly increased. Finally, the major initial reduction product, ketone **14**, was progressively replaced by naphthalene (**8**). Compared with **8**, tetralin was never as significant a product from **2-N** as from **1-N**, although traces could be detected at long reaction times.

Binaphthol **4** (1.06 mmol in a 6.8-mL tube) was heated at 400 °C for 1 h. One-half was consumed to give not only the corresponding cyclized product **3** but also **2-N** in a molar ratio of 0.6:1.0. Note that this cyclization is much more sluggish than that of binaphthol **2** with a comparatively greater reversion to the parent naphthol. Similar heating of **3** for periods up to 64 h gave no detectable change.

Dilution with *m*-terphenyl led to a decrease in initial rate similar to that for **1-N**, although less data were collected for **2-N**. For example, after 16 h at 400 °C, conversion decreased from 17% for the neat liquid (Table III) to 3.6% for a solution ($x = 0.20$) in *m*-terphenyl. In contrast, a comparable solution ($x = 0.20$) in benzophenone showed 43% conversion in this period. Again the normally observed reduced products from **2-N** were replaced by diphenylmethane. Interestingly, the condensed products were almost entirely the symmetrical ones **3** and **4**. Data are summarized in Table IV.

Discussion

The dominant final products from extended thermolysis of the naphthols at 400 °C result from a *condensation* to form dinaphthofurans and a *dehydroxylation* to form naphthalene, whereas there is no evidence for *decarbonylation* in this temperature range where thermal reactivity is first manifested. However, these final products conceal the character of the initial thermolysis reactions and the mechanistic coupling between condensation and dehydroxylation.

The increase in the ratio of dinaphthofuran **3**/binaphthol **4** derived from **2-N** from ≤0.04 at 1% conversion to ≳ 15 at 20–25% conversion (Table III) is the clearest evidence that binaphthols are the dominant precursors of the final cyclized furans. An analogous increase in the ratio of dinaphthofuran **1**/binaphthol **2** from **1-N** with increasing reaction time (Table I) points to the same conclusion, although in this case, more furan was already present at the lowest conversion experimentally studied. Such a difference in behavior can be easily rationalized from the observation made in control experiments that cyclization of binaphthol **4** was much slower than that of **2**. (We comment further below on the partial reversion to naphthol which accompanied these thermal cyclizations.) This rate difference probably results from the severe steric crowding present in dinaphthofuran **3** compared with the other isomers. We have estimated the internuclear distance between H-1 and H-13 in a hypothetically planar form of **3** to be only 65–70 pm on the basis of addition of two regular aromatic hexagons to the known structure[42] of dibenzofuran; hence, clearly **3** must be distorted from planarity although probably not as seriously as dibenzo[*c*,*g*]phenanthrene.[43] Although we have not experimentally demonstrated that dinaphthofuran **5** from **2N** also has a binaphthol (**16**) as its dominant precursor because we have not yet had **16** in hand, there is no strong reason to believe otherwise, provided **16** undergoes cyclization more rapidly than **4**. In summary then, we can focus mechanistic questions concerning the *condensation* process onto the mode of formation of an aromatic C–C bond regioselectively ortho to the hydroxy group in the starting naphthol.

The equivalent of hydrogen made available by this conversion of two molecules of naphthol to a binaphthol is not released as molecular hydrogen but rather is somehow transferred to a third molecule of naphthol to effect reduction, largely of the substituted ring to form 1(2)-tetralone (**6** or **14**; presumably from ketonization of a dihydronaphthol) and, to a lesser but measurable extent, of the unsubstituted ring to form 5,6,7,8-tetrahydro-1-(2)-naphthol (**7** or **15**). Hence the most simplified representation of the initial reactions is given in eq 1 and 2 (Scheme I), which are focused on major products. The second mechanistic question which is then defined is the nature of this unusual hydrogen transfer.

The product behavior from **2-N** raises still an additional mechanistic restriction because the ratio of C_1–$C_{1'}$ coupling (to produce binaphthol **4** and ultimately dinaphthofuran **3**) to C_1–$C_{3'}$ coupling (to produce presumably **16** and ultimately **5**) is conversion dependent.[44] Dinaphthofuran **3** was stable at 400 °C and, in particular, gave no isomerization to **5**. Thermolysis of the precursor binaphthol **4** gave the expected furan **3**; however, the partial reversion to **2-N** which accompanied this cyclization may offer a route for apparent "isomerization" from the symmetrical to the unsymmetrical product series (see below).

The secondary conversions of the tetralone products to naphthalene and tetralin presumably result because these ketones are better hydrogen acceptors than the naphthols themselves (compare results with benzophenone). Although we have not investigated this chemistry in detail, further hydrogenation to tetralols followed by rapid de-

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(42) Dideberg, O.; Dupont, L.; Andre, J. M. *Acta Crystallogr. Sect. B* **1972**, *28*, 1002. Banerjee, A. *Ibid.* **1973**, *29*, 2070.

(43) McIntosh, A. O.; Roberton, J. M.; Vand, V. *J. Chem. Soc.* **1954**, 1661.

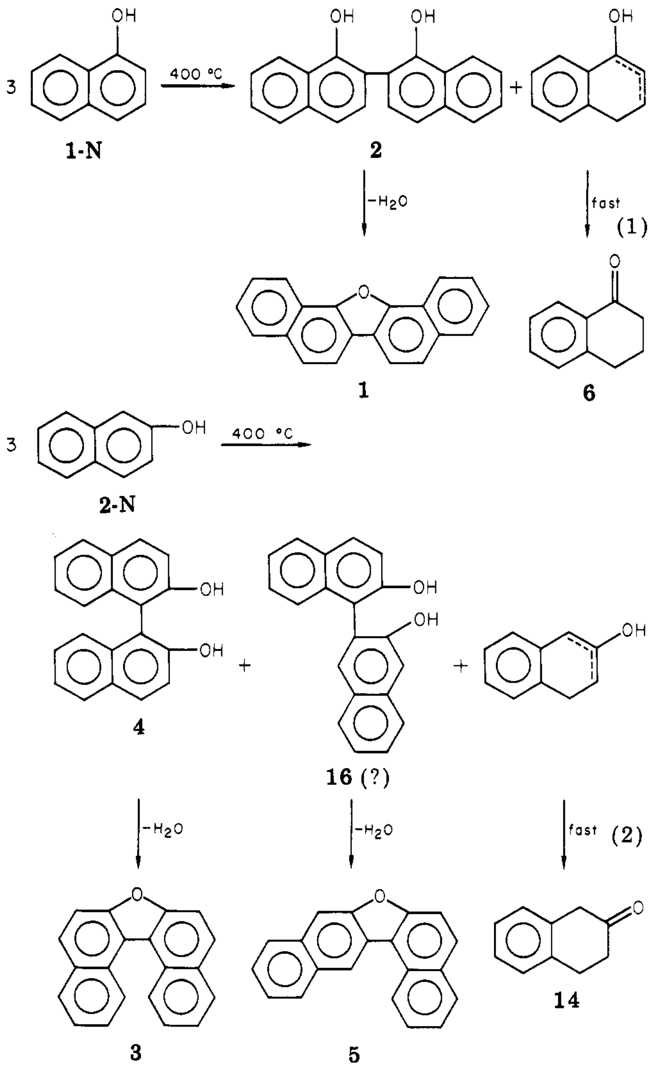
(44) At very long reaction times (112 h at 400 °C) for **2-N**, still a third product with *m*/*z* 268 is found by GC–MS which could be the furan from C_3–$C_{3'}$ coupling.

Table IV. Effect of Diluents on Thermolysis of 2-Naphthol[a]

diluent	concn of 2-N (x)	% conversion[c] to (2-N equivalents[b]) 3	4	5	16	14	15	8	13	Ph_2CH_2	Σ[d]
none[e,f]	1.00	5.9	0.3	6.9	0.2	1.9	1.0	0.8	13.8		17.1
m-terphenyl	0.20	0.3	1.5	0.5	0.1	1.0	0.1	0.2	0.2		3.6
benzophenone	0.20	14.5	26.6	1.7		0.1				g	42.9

[a] 400 °C for 16 h. [b] See footnote *c*, Table I. [c] See footnote *e*, Table III. [d] Excluding **13**. [e] See Table III. [f] 16.25 h. [g] (**3** + **4** + **5**)/Ph_2CH_2 = 2.1 (molar ratio).

Scheme I



hydration and dehydrogenation and/or disproportionation of dihydronaphthalenes does not seem unreasonable.

The fact that naphthol thermolysis in the gas phase gave very similar product distributions suggests that the reaction can occur under nonpolar conditions and does not specifically require the somewhat polar liquid regime provided by neat naphthol. In fact, if the liquid-phase rate data in Figure 1 (see below) are extrapolated, in concentration units based on an estimated liquid **1-N** density, to the gas phase, the (somewhat scattered) gas-phase initial rates cluster around the extrapolated linear correlation. Thus, although the quantitative variability of the gas-phase data precludes any more detailed conclusions, we do not see evidence for a strong effect of polarity of the reaction medium.

If the liquid-phase data for **1-N** conversion vs. time (Table I) are plotted in integral fashion for various kinetic orders, an order between 2 and 3 is indicated. However, we consider this procedure questionable for a reaction obviously consisting of several consecutive steps because of possibilities of acceleration or inhibition by products at long reaction times. Therefore, we regard the initial rate data as a function of dilution (Table II) inherently more reliable. Again an order between second and third is indicated (Figure 1).[45] Such behavior is suggestive of a rate law of the general form shown in eq 3 for the situation

$$2\ \mathbf{1\text{-}N} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X \underset{\mathbf{1\text{-}N}}{\overset{k_2}{\rightarrow}} \text{products}$$

$$\text{rate} = [k_1k_2(\mathbf{1\text{-}N})^3]/[k_{-1} + k_2(\mathbf{1\text{-}N})] \qquad (3)$$

where two molecules of **1-N** interact to form some transient intermediate X which decays competitively either by reversal or by interaction with further **1-N**. Although a plot of such a function in the format of Figure 1 would not be linear, the extent of curvature expected over the range of concentration studied herein is scarcely larger than the experimental uncertainty.

Added benzophenone not only accelerated the condensation portion of the naphthol thermolysis but also eliminated the reduction portion in favor of almost exclusive formation of diphenylmethane. The initial stoichiometry of eq 1 and 2 was replaced by that of eq 4. Hence, benzophenone must be able to intervene in the mechanism at a kinetically significant stage and thereby to decouple condensation from hydrogen transfer.

$$2C_{10}H_7OH + 0.5Ph_2C{=}O \rightarrow (HOC_{10}H_6\text{–})_2 + 0.5Ph_2CH_2 + 0.5H_2O \qquad (4)$$

Although assignment of a specific mechanism is still premature based on the data in hand, we will briefly explore two working hypotheses as the basis for further studies. Since biphenols are characteristic products from the coupling of phenoxy radicals,[46] and since hydrogen atom transfers provide a very natural rationalization for the hydrogen transfer part of the thermolyses, we consider first the probability and consequences of proposing free-radical intermediates. The weakest bond in phenol is the O–H bond with a bond dissociation energy, $D°_{298K} \simeq 86.5$ kcal/mol.[47] If we estimate a further weakening of ~3.5 kcal/mol for **1-N**,[48] we arrive at $D°_{298K}$ ($1\text{-}C_{10}H_7O\text{–}H$) $\simeq$ 83 kcal/mol. Using an estimate of an A factor for O–H homolysis of 10^{16} s^{-1},[49] we can then estimate for simple

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(45) As pointed out in the text, varying mixtures of **1-N** and *m*-terphenyl will not be of constant polarity. Therefore, in the absence of separate probes of response of the reaction to solvent polarity, a modest polarity effect superimposed on a dominant kinetic-order effect cannot be rigorously eliminated.

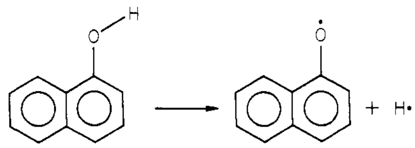
(46) Musso, H. In "Oxidative Coupling of Phenols"; Taylor W. I., Battersby, A. R., Eds.; Marcel Dekker: New York, 1967; Chapter 1.

(47) Colussi, A. J.; Zabel, F.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 161.

(48) (a) Mahoney, L. R.; DaRooge, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 4722. (b) This estimate is consistent with one based on the corresponding difference in resonance energies between benzyl and 1-naphthylmethyl radicals: McMillen, D. F.; Trevor, P. L.; Golden, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 7400. (c) Herndon, W. C.; *J. Org. Chem.* **1981**, *46*, 2119.

(49) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976.

homolysis, step 5, at 400 °C a half-life ~2000 years.[50] Clearly, unimolecular homolysis cannot be a source of 1-naphthoxy radical (**17**), nor is the observed absence of hydrogen formation consistent with any postulate involving free hydrogen atoms because hydrogen abstraction from naphthols should be extremely facile.



(5)

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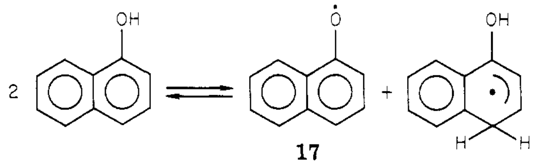
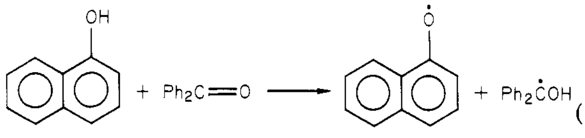
However, generation of radicals by a bimolecular hydrogen transfer[51,52] as shown in eq 6 might be much more rapid if the penalty in *A* factor for such a bimolecular process could be overcompensated by a more favorable E_a. The enthalpy of concerted step 6 will be lower than that of step 5 by an amount corresponding to the enthalpy of addition of hydrogen atom to **1-N**. Addition of hydrogen atom to benzene can be estimated from currently accepted heats of formation[49] to be exothermic by 22 kcal/mol. Addition to naphthalene should be even more exothermic by an additional ~6 kcal/mol on the basis of recent correlations[48c] of radical resonance energies. Using the ~10 kcal/mol difference in $D°$ values for the C–H bonds in methane and dimethyl ether[53] as a guide to the difference in stabilization of a localized radical by H and OH substituents and somewhat arbitrarily assigning one-half this difference to a delocalized hydroxyl-substituted radical such as **18**, we estimate still an additional ~5 kcal/mol exothermicity in adding hydrogen atom to **1-N** rather than to naphthalene. Thus, we finally estimate the enthalpy of step 6 to be ~[83 - (22 + 6 + 5)] ≃ 50 kcal/mol. Since its reverse is simply a radical disproportionation for which negligible activation energy would be expected, this approximation procedure also gives ~50 kcal/mol as the activation energy for step 6. Quantitative thermochemical estimation of an *A* factor for step 6 would require estimates of $S°$ (**17**) and $S°$ (**18**). Sufficient input data do not exist but *A* factors for similar hydrogen transfers[52] fall in the range 10^{10}–10^{11} M^{-1} s^{-1}. We can then finally estimate a $t_{1/2}$ for step 6 and a **1-N** concentration of ~4 M (liquid phase) as ~12–120 h. This differs from the observed consumption rate of **1-N** (Table I) by a factor of only ~4–40. Thus, within the accuracy of such estimation procedures,[50] step 6 cannot be summarily dismissed on thermochemical kinetic grounds and deserves serious consideration in further studies. The accelerating and product-diverting role of benzophenone would then result from competitive incursion of step 7, which would be favored over step 6 by the more favorable exothermicity of (formal) addition of hydrogen atom to benzophenone.



(6)

17 **18**



(7)

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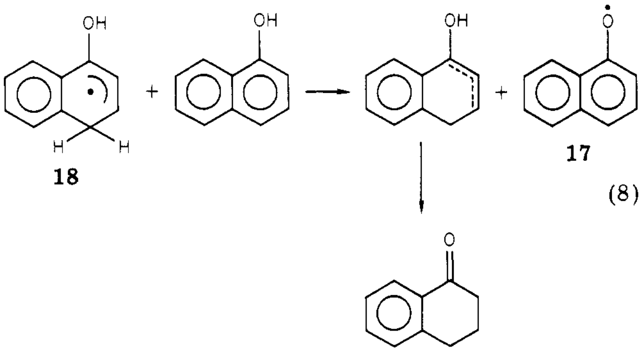
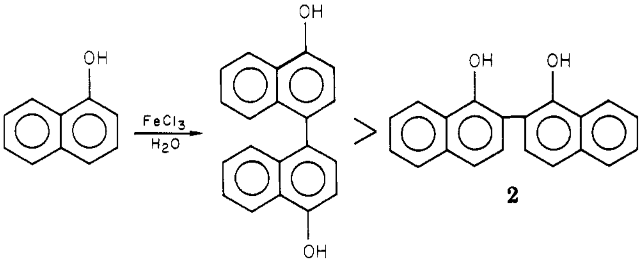
Abstraction of hydrogen by radical **18** from **1-N** (step 8 then forms a very natural route for production of tetralone and completes the hydrogen-transfer process. If coupling of two 1-naphthoxy radicals then were to give largely binaphthol **2**, the sum of steps 6, 8, and 9 would constitute the required dominant stoichiometry shown in eq 1. Although this sequence is not exactly homologous to kinetic sequence 3, in essence, radical **18** corresponds to intermediate X which is consumed either by the reversal of step 6 or by capture by additional **1-N** in step 8.



18 **17** (8) **6**

$$2\,\mathbf{17} \xrightarrow{?} \mathbf{2} \qquad (9)$$

The regioselectivity demanded of radical coupling step 9 poses, however, an apparent problem. Oxidative coupling of **1-N** with one-electron oxidants such as Fe(III) in aqueous media gives a preponderance of binaphthol **12** over binaphthol **2**,[27] in a process generally believed[46] to involve naphthoxy radicals. Binaphthol **12** also predominated in the reaction of **1-N** with benzoyl peroxide in refluxing chloroform.[54] This regioselectivity parallels the values of the observed hfs constants in the ESR spectrum of 1-naphthoxy radical: $a_{4\text{-H}} > a_{2\text{-H}}$.[55] In constrast, the initial ratio of **12**/**2** from thermolysis of **1-N** at 400 °C is ≲0.05. Does such a contrast in regioselectivity eliminate from consideration naphthoxy radicals as the source of the binaphthols in the thermal reaction, or is such a change



12 **2**

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(50) In this and subsequent approximate thermochemical estimates, we have made no attempt to estimate the small effects of differential heat capacities between 298 K and 673 K because the inherent accuracy of the estimates of *A* and E_a themselves are not accurate enough to warrant the attempted correction. For the same reason, we have not included the small changes in thermochemical quantities resulting from changes from gas to liquid standard states for $\Delta n \neq 0$.

(51) Step 6 is analogous to the often proposed process for the third-order thermal initiation of styrene polymerization: Graham, W. D.; Green, J. G.; Pryor, W. A. *J. Org. Chem.* **1979**, *44*, 907.

(52) Benson, S. W. *Int. J. Chem. Kinet.* **1980**, *12*, 755. Ayranci, G.; Back, M. H. *Ibid.* **1981**, *13*, 897. Delliste, D.; Richard, C.; Martin, R. *J. Chim. Phys. Phys.-Chim. Biol.* **1981**, *78*, 655.

(53) Cruickshank, F. R.; Benson, S. W. *Int. J. Chem. Kinet.* **1969**, *1*, 381.

(54) Chauhan, Y. S.; Mathur, K. B. L. *Indian J. Chem.* **1975**, *13*, 38.

(55) Dixon, W. T.; Foster, W. E. J.; Murphy, D. *J. Chem. Soc., Perkin Trans. 2* **1973**, 2124.

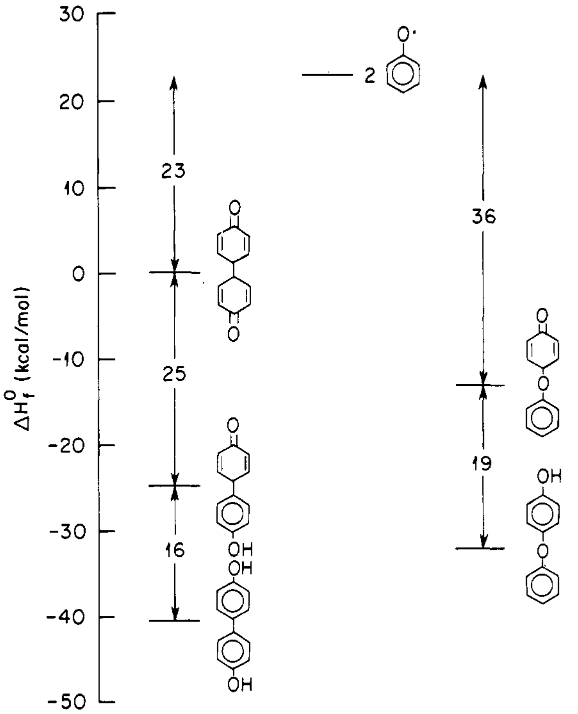


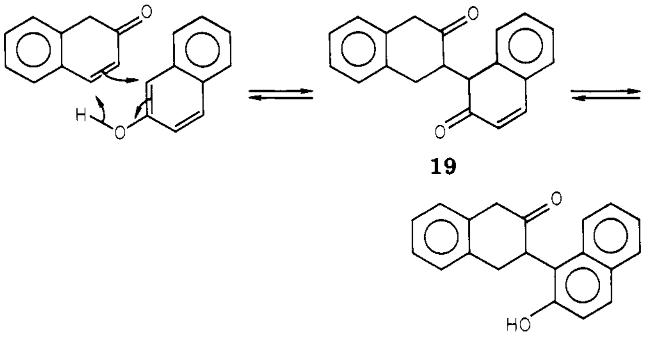
Figure 3. Approximate energetics of some competitive coupling pathways of phenoxy radicals.

in regioselectivity at high temperature possible? We now point out why the latter possibility deserves attention.

For purposes of illustration, the coupling of simple phenoxy radicals is shown in Figure 3 for only two possibilities, C_{para}–C_{para} and C_{para}–O. Note that each coupling is a multistep process which must pass through cyclohexadienone intermediates. On the basis of the group additivity approach,[49] we show in Figure 3 estimates of the heats of formation of the various species involved. Thus, although C–C coupling overall is exothermic by ~65 kcal/mol (~60 kcal/mol for 2 **17** → **2** or **12**), this process must occur in three successive steps, each of which is exothermic by only ~20–25 kcal/mol. Similar thermochemical estimates have been made by Mahoney and Wiener[56] and by McMillan and co-workers.[57] A consequence of this energy profile is that the initial coupling steps at high temperature might be highly reversible with the overall coupling rate being determined by subsequent enolization. This possibility was, in fact, recognized and experimentally demonstrated by Mahoney and Wiener[56] for certain phenoxy radicals in chlorobenzene solution even at ambient temperatures. Although the details of possible enolization pathways are not known with certainty,[57] they are likely to involve bimolecular steps with *A* factors less than that for unimolecular homolysis. Hence, increasing reversibility with increasing temperature would not be unexpected. For illustration of the inherent thermal instability of the initial coupling products, note that bond-dissociation energies of 23 and 36 kcal/mol (see Figure 3) correspond at 400 °C to half-lives ($A \sim 10^{15}$ s^{-1}) of only 20 ns and 340 μs, respectively. Additional evidence for the thermal lability of such cyclohexadienone intermediates comes from studies[58] of the redistribution of *p*-phenoxyphenol "dimers" to "monomer" and polymer; facile homolysis of quinone ketals has been proposed as a key step in this reaction.

The observation that thermolysis of binaphthols **2**, **4**, and **12** all led to some formation of the parent naphthol (in addition to furan formation in the first two cases) lends credence to the idea that, in fact, the *entire* coupling scheme may be somewhat reversible at 400 °C. If naphthoxy radicals are formed during the control thermolyses of binaphthols, their capture by hydrogen abstraction from the excess binaphthol would produce naphthol, as observed, but would interrupt the possibility of their recoupling with a different regiochemistry. The idea that thermolysis of a phenolic substance such as **12** could occur with a facility unexpected from its very strong aryl–aryl C–C bond because of prior enolization to an isomer containing a much weaker bond has been demonstrated in a different system by McMillan and co-workers.[57] In conclusion then, we could well imagine a situation where the regioselectivity of coupling of naphthoxy radicals at high temperatures is determined not by the regioselectivity of the kinetically preferred initial coupling site but by subtle differences in rates of enolization, compounded by the situation where one set of isomers (coupling ortho to the hydroxyl group) is constantly being drained off by formation of the kinetically stable furans. Similarly, subtle differences in relative rates of enolization, cyclization, and bond rupture of intermediates in the C_1–$C_{1'}$ vs. C_1–$C_{3'}$ coupling pathways from **2-N** might account for the variation in the product ratio (**3** + **4**)/(**5** + **16**) with reaction time. Further speculation[59] is not meaningful in the absence of experimental data for naphthoxy radicals generated under these conditions from an authentic source. Nevertheless, we believe that the free-radical hypothesis for naphthol thermolysis, while far from demonstrated, deserves serious further attention.

An alternate mechanistic hypothesis which more neatly rationalizes the ortho regioselectivity is an ene-type condensation[60] between one molecule of parent naphthol and another in its keto form to give a dihydro derivative of a binaphthol. This is illustrated below for the case of C_1–$C_{3'}$ coupling of **2-N**:



19

20

However, this approach demands that species such as **19** and/or **20**, which would be identified with species X in eq 3, not accumulate but be rapidly dehydrogenated by further 2-N, a process for which we find no ready analogy.

The contrast between the coupled *condensation* and *dehydroxylation* behavior observed here at 400 °C and the *decarbonylation* observed at 900 °C[33] demonstrates that the former must have a lower overall enthalpy of activation

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(56) Mahoney, L. R.; Wiener, S. A. *J. Am. Chem. Soc.* **1972**, *94*, 585.

(57) McMillan, D. F.; Ogier, W. C.; Ross, D. S. *J. Org. Chem.* **1981**, *46*, 3322.

(58) Bolon, D. A. *J. Org. Chem.* **1967**, *32*, 1584. Cooper, G. D.; Blanchard, H. S.; Endres, G. F.; Finkbeiner, H. *J. Am. Chem. Soc.* **1965**, *87*, 3998.

(59) For example, we cannot rule out the possibility of rearrangement pathways of the Cope and Claisen type; we thank Drs. McMillan and Ogier[57] for this suggestion.

(60) Hoffmann, H. M. R. *Angew. Chem., Int. Edn. Engl.* **1969**, *8*, 556. Metzger, J.; Köll, P. *Ibid.* **1979**, *18*, 70.

than decarbonylation but a less favorable entropy of activation so that a temperature-dependent crossover in behavior can occur where $\Delta H^\ddagger = T\Delta S^\ddagger$.

The rates of the liquid-phase naphthol reactions at 400 °C are rapid enough to qualify as models for possible reactions of phenolic groups under coal liquefaction conditions at, say, 450 °C for 30–60 min.[8] In this context, the reactions described herein may well be a mixed blessing. To the degree that they ultimately convert ca. one-third of the phenol to an arene and convert ca. two-thirds of the oxygen content of the phenol to water, they are desirable. However, to the degree they form furans of larger size containing a form of oxygen even more difficult to remove in later hydro treating,[61] they appear undesirable. Cross-reaction between phenolic groups in coal and those in the process solvent could lead to grafting of solvent to coal with accompanying solvent loss. For the pure naphthols themselves, the condensation (hydrogen-donating) and dehydroxylation (hydrogen-accepting) processes are intimately coupled in a stoichiometrically determined ratio. In the much more complex environment of coal liquefaction, they need not be. For example, our results with benzophenone illustrate how a better hydrogen acceptor can take over the hydrogen-accepting role to leave the naphthol playing only a donor role and forming the furan. It remains to be demonstrated whether good hydrogen donors can reverse this scenario so as to maximize the dehydroxylation process.[62]

The high kinetic order of the reactions described herein suggests that their possible involvement during liquefaction deserves most attention under conditions of the highest phenol concentrations. For example, furan formation may be one contribution to the retrogressive char-forming reactions reported[63] for liquefaction in solvents rich in phenolic functionality. Other, more desirable reactions of phenols which are of lower kinetic order might therefore be of relatively more importance at lower phenolic concentration.

Experimental Section

Materials. Compounds subjected to thermolysis were prepared and/or purified as follows. 1-Naphthol and 2-naphthol were repeatedly sublimed at ~90 °C and ~6 Pa until free from yellow color; they were then crystallized twice from aqueous acetic acid and once from cyclohexane before being sublimed a final time. The bis(naphthyl) ethers **11** and **13** were prepared by heating the naphthols with potassium hydrogen sulfate at ~200 °C;[64] the base-insoluble residues were chromatographed on neutral alumina with benzene eluant and the ether products were crystallized from hexane or benzene. A suspension of **1-N** in water was oxidatively coupled with ferric chloride at ~80 °C.[27] The portion of the crude product insoluble in hot benzene was crystallized from 95% ethanol to give binaphthol **12**. The benzene-soluble portion was chromatographed over Florisil; crystallization from ethanol–water of the material eluted by benzene gave binaphthol **2**. Binaphthol **4** was commercially available. *m*-Terphenyl was refluxed (~365 °C) under argon for 18 h and then crystallized 3 times from ethanol. Benzophenone was distilled under reduced pressure.

Additional materials needed for GC and MS calibration were obtained as follows. 1-Tetralone (**6**), 1-tetralol (**10**), and 5,6,7,8-tetrahydro-1-naphthol (**7**) were commercially available. Reduction of **2-N** with sodium in refluxing *n*-amyl alcohol[65] gave a mixture of 2-tetralol and 5,6,7,8-tetrahydro-2-naphthol (**15**), which were separated by base extraction and purified by distillation. Oxidation of 2-tetralol gave 2-tetralone (**14**). An authentic sample of dinaphthofuran **1** was isolated from a thermolysis run of **1-N** at 400 °C for 25.7 h by fractional sublimation and crystallization from ethanol, mp 178–180 °C (lit.[21] mp 180–181 °C). The unsymmetrical dinaphthofuran **5** was isolated from a thermolysis run of **2-N** at 400 °C for 73 h by elution from neutral alumina with benzene–hexane (1:3) and crystallization from benzene, mp 158–159 °C (lit.[23] mp 158–159 °C). The symmetrical dinaphthofuran **3** was prepared by heating binaphthol **4** with 2.6 times its weight of potassium hydrogen sulfate in an open tube at ~200 °C for 3 h; after digestion with boiling aqueous sodium hydroxide, the benzene-soluble portion was chromatographed over neutral alumina in benzene and the eluate crystallized from benzene, mp 155–156 °C (lit.[23] mp 156 °C). The distinction between the three isomers was made by NMR as discussed in the Results section.

Thermolysis Procedure. Pyrex Carius combustion tubes were washed with detergent, rinsed extensively with distilled water, acetone, and distilled water again, dried at 150 °C, and stored over molecular sieve dessicant. The appropriate amounts of materials to be thermolyzed were weighed into a tube which was then subjected to three "freeze–thaw" degassing cycles under inert gas and sealed at <1 Pa. Consideration of the weight and total volume of the sealed tube and the density of Pyrex gave the internal volume, typically 6.8 mL. Extrapolation of data[37] from lower temperatures suggest the vapor pressures of **1-N** and **2-N** at 400 °C to be ~950 and ~850 kPa, respectively. Thus, for a typical charge of 4.8 mmol of **1-N** in a 6.8-mL tube and assuming ideal gas behavior, we estimate ~76% to be in the liquid phase in equilibrium with its vapor at ~950 kPa. The corresponding estimate for a typical charge of 4.6 mmol of **2-N** in a 6.8-mL tube is 78% in the liquid phase in equilibrium with its vapor at ~850 kPa. Tubes were heated in a horizontal position in a thermostated fluidized sand bath; temperature was monitored by a thermocouple placed in an empty tube and positioned adjacent to the reaction tube. After the desired reaction time, tubes were quickly cooled with flowing air. They were then opened while cooled in liquid nitrogen, and benzene or acetone containing a known amount of internal standard for GC analysis (usually *n*-propylbenzene) was added to dissolve the contents before analysis.

Product Identification. From **1-N**, dinaphthofuran **1**, 1-tetralone (**6**), 5,6,7,8-tetrahydro-1-naphthol (**7**), bis(1-naphthyl) ether (**11**), naphthalene (**8**), tetralin, indan, and 1-methylindan were identified from GC–MS (70 eV) spectra of reaction mixtures compared with spectra of authentic samples. Binaphthols **2** and **12** were similarly identified after trimethylsilylation (see below). Two trace products gave *m/z* 342 after trimethylsilylation and thus are probably naphthylnaphthols, but positive identification has not been achieved. Two additional trace products with retention times slightly shorter than the furan remain unidentified. Trace amounts of a material with the correct retention time for 1-tetralol (**10**) were occasionally observed.

From **2-N**, dinaphthofurans **3** and **5**, 2-tetralone (**14**), 5,6,7,8-tetrahydro-2-naphthol (**15**), bis(2-naphthyl) ether (**13**), and naphthalene (**8**) were identified by GC–MS comparison to authentic materials. Binaphthol **4** was similarly identified after trimethylsilylation. A persistent trace material observed only after trimethylsilylation had *m/z* 430 and is suspected to be 1,3′-binaphthalene-2,2′-diol (**16**), but no rigorous identification has been made for this unreported material.

Analytical Procedure. Benzene solutions of the thermolysis products from **1-N** were analyzed by GC directly, after extraction with dilute aqueous base, and after trimethylsilylation. Typically, the reaction mixture from 650–750 mg of **1-N** was dissolved in 10 mL of benzene containing internal standard. A 5-mL aliquot was extracted with 15 mL of 1 N sodium hydroxide solution. A 4-mL aliquot was treated with 2 mL of a reagent solution prepared from bis(trimethylsilyl)trifluoroacetamide–1% trimethylsilyl chloride and pyridine (1:2, w/v) and heated 30 min on a steam bath. GC analyses were performed on a $^1/_8$-in. 4% Dexsil 300 column, temperature programmed from 80 to 335 °C at 8 °C/min,

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[61] Rollmann, L. D. *J. Catal.* **1977**, *46*, 243.

[62] It has been reported that heating ~10 mol % solutions of **1-N** in hydrogen-donor solvents such as tetralin at 450 °C gave naphthalene as the only detected product. However, it is not clear whether the analytical procedures used would have detected furan **1**; Cronauer, D. C.; Jewell, D. M.; Shah, Y. T.; Modi, R. J. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 153.

[63] Derbyshire, F. J. *Proc., 6th Ann. EPRI Contractors' Conf. Coal Liquefaction* **1981**, 5-1.

[64] Clowes, G. A. *J. Chem. Soc. C* **1968**, 2519.

[65] Bamberger, C.; Lodter, W. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 197. Bamberger, C.; Kitschelt, M. *Ibid.* **1890**, *23*, 885.

with a flame-ionization detector. Analysis of the parent solution gave values for **1**, the sum of **6** and **7**, **11**, **8**, tetralin, and 1-tetralol (?). In runs containing benzophenone, the formation of diphenylmethane was also monitored. Analysis after base extraction to remove all phenolic components gave the most reliable value for **6**. Analysis after trimethylsilylation gave values for **2** and **12** and the most reliable value for **7**. The binaphthols were detected only after trimethylsilylation because they apparently react with the Dexsil stationary phase before eluting. All peak areas were determined with a planimeter and were converted to molar amounts on the basis of an internal standard and calibration factors determined with authentic samples.

A similar procedure was used for **2-N** thermolyses except that acetone was used as solvent. The base-extraction step was omitted and acetone was gently evaporated from an aliquot before trimethylsilylation. GC analyses were performed on an OV-101 WCOT column, temperature programmed from 75 to 280 °C at 12 °C/min. Direct analysis gave values for all products except the binaphthols, which were determined after trimethylsilylation. Peak areas were determined by electronic integration.

Occasional checks for formation of noncondensable gas were made. The reaction tube, before opening, was attached with plastic tubing to a manometer and the closed system was evacuated. With the lower portion of the tube cooled in dry ice-acetone, the tip was crushed through the plastic tubing. No significant increases in pressure were noted. For occasional measurements of water formation, reaction mixtures were dissolved in dioxane containing 2-propanol as an internal standard. GC analysis for water and 2-propanol was performed on a Poropak Q column with a thermal conductivity detector.

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Registry No. 1, 831-82-3; **2**, 604-60-4; **3**, 239-69-0; **4**, 602-09-5; **5**, 204-91-1; **6**, 604-60-4; **7**, 529-35-1; **8**, 91-20-3; **9**, 119-64-2; **10**, 529-33-9; **11**, 607-52-3; **12**, 1446-34-0; **13**, 613-80-9; **14**, 530-93-8; **15**, 1125-78-6; **16**, 82495-18-9; Ph$_2$CH$_2$, 103-29-7; benzophenone, 119-61-9; 1,1′-Dioxo-4,4′-bis[2,5-cyclohexadiene], 82495-19-0; 4′-hydroxy-4-phenyl-2,5-cyclohexidien-1-one, 82495-20-3; 1,1′-biphenyl-4,4′-diol, 2122-46-5; 4-phenoxyphenol, 831-82-3; 4-phenoxy-2,5-cyclohexadien-1-one, 82495-21-4.

Cyclopropene Photochemistry. Mechanistic and Exploratory Organic Photochemistry[1,2]

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Four new cyclopropenes have been synthesized and their photochemistry has been investigated. Thus, 3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene was found on direct photolysis to afford four photoproducts, the two major products of which derived from novel photochemistry. 2-Methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0.^{1,5}0^{4,6}]undeca-8,10-diene derived from [2 + 2] cycloaddition of the excited cyclopropenyl π bond to the C-1,C-2 π bond of the phenyl of the 2-phenylallyl side chain. The quantum yield for this novel transformation was 0.023. A second photoproduct was 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane. This product results from a formal [2 + 2] cycloaddition of the excited cyclopropenyl π bond to the allyl double bond. A diradical mechanism is structurally equivalent. Formation of such a tricyclic [2.2.0.0^{2,6}] system is normally not found in direct irradiations. The quantum yield for this product was 0.088. Also formed was 3-methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene with an efficiency of 0.019. This product is understood as deriving either (i) from cyclopropene opening to a carbene which then adds to the allyl π bond or (ii) from a bicyclic diradical arising from vinyl-vinyl bonding. The fourth photoproduct is 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene. The efficiency was 0.018. The bicyclic diradical above provides a common species leading to the last three products. Sensitization led only to the first two products: the tetracyclic diene (ϕ = 0.26) and the tricyclo[2.2.0.0^{2,6}]hexane (ϕ = 0.15). Product structures were established by X-ray, degradation, independent synthesis, and spectral analysis. In addition, the photochemistry of *cis*- and *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene was investigated. Stereoisomerization resulted from the singlet but not the triplet. Mechanisms for the above transformations are considered. Finally, corresponding thermal chemistry exhibited by the above compounds was investigated.

Introduction

In our previous studies,[2b,3] we reported the photochemical transformation of vinylcyclopropenes to afford cyclopentadienes. Similarly, Padwa[4,5] has investigated the photochemical behavior of vinyl[4] and allyl[5] cyclopropenes. Cyclopropene photochemistry has been unusual in the rich variety of different types of photochemical transformations encountered.

Our present research began with an investigation of the photochemistry of 3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene (**1**). Additionally, the photochemistry

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(1) (a) This is paper 134 of our photochemical series. (b) It is paper 5 of our series on "Cyclopropene Photochemistry". See ref 2f for our last paper on cyclopropene chemistry.

(2) (a) For paper 129, note Zimmerman, H. E. *Tetrahedron* **1982**, *38*, 753–758. (b) For an earlier publication on cyclopropene chemistry, see Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331–2345. (c) Publication 130: Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Chapter 16. (d) Paper 131: Zimmerman, H. E.; Penn, J. H.; Carpenter, C. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 2128–2132. (e) Publication 132: Zimmerman, H. E. *Top. Curr. Chem.* **1982**, *100*, 45–73. (f) Paper 133: Zimmerman, H. E.; Kreil, D. J. *J. Org. Chem.* **1982**, *47*, 2060–2075.

(3) (a) Zimmerman, H. E.; Aasen, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 2342–2344. (b) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493–1506.

(4) (a) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N. *J. Am. Chem. Soc.* **1977**, *99*, 2344–2345. (b) *J. Org. Chem.* **1978**, *43*, 1481–1492. (c) For a general review of more recent papers by these authors, note Padwa, A. *Org. Photochem.* **1979**, *4*, 261–326.

(5) (a) Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2345–2347. (b) For a very recent paper with references to intervening literature, see Padwa, A.; Blacklock, T. J.; Cordova, D. M.; Loza, R. *Ibid.* **1980**, *102*, 5648–5656.

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