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Mechanisms of Condensation of Biaryl Hydrocarbons

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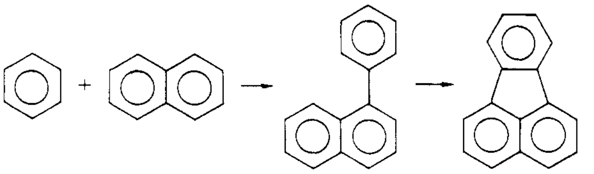
Results of kinetic studies of the condensed phase thermal reactions of the following biaryl hydrocarbons are reported; 1,1′-binaphthyl, 1,2′-binaphthyl, 1-phenylnaphthalene, and 9-phenylanthracene. Condensation generally occurred in parallel with both isomerization and dissociation and rates depended on concentrations of hydrogen donors. In order to simplify mechanisms, detailed studies used donors capable of providing just one H atom. These were xanthene, fluorene, and diphenylmethane. Condensation of 1,1′-binaphthyl in the presence of xanthene, the most effective donor, followed a second-order rate law (first order in both xanthene and binaphthyl concentration), $k/\mathrm{M}^{-1}\,\mathrm{s}^{-1} = 10^{5.9\pm0.6}\exp(-36.0 \pm 2.0\ \mathrm{kcal}/RT)$ (360–560 °C). Fluorene was one-fifth as effective as xanthene while diphenylmethane was nearly inert. A mechanism is proposed in which the key intermediates in all reactions are radicals created by H-atom transfer to the biaryls. In the condensation of naphthyl-containing biaryls, it is suggested that reactions are initiated by H transfer to a position next to the condensation site. Details of the unimolecular steps leading to condensation and isomerization, however, remain unclear. Over the conditions studied, the reaction order with respect to donor varied between one and zero. It is proposed that this variability is a result of competition between two pathways for H transfer, one involving a simple, selective H transfer from the donor to a biaryl molecule, the other involving a free H-atom intermediate.

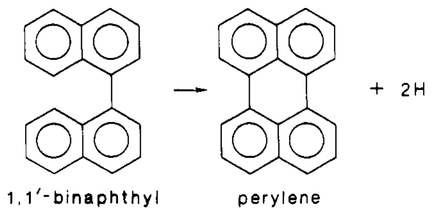
Introduction

Condensed polycyclic aromatic hydrocarbons (CPAH) are ubiquitous products of hydrocarbon pyrolysis. While there has been considerable recent work on the detection of these substances in process effluents and in the environment,[1] relatively few studies have been reported on the elucidation of their formation mechanisms in well-controlled reaction systems. Moreover, most mechanistic studies of these reactions have been done prior to the advent of modern chromatographic techniques and before the development of the methods of "thermochemical kinetics".[2] In this work, we use these two tools to examine reactions leading to the formation of CPAH.

Because of their ease of formation and their stability toward dissociation, biaryl hydrocarbons are plausible precursors of many CPAH formed in incomplete combustion and pyrolysis. These reactions have long been known to occur in the laboratory.[3,4] A general mechanism leading to CPAH is outlined in eq 1.


(1)

In the present work, we have determined the kinetic behavior of reactions 2–5 near 440 °C in the condensed phase. The parallel processes leading to isomerization and dissociation were also examined. Farnum et al.[5] have given a preliminary account of their studies of biaryl condensation reactions, including reactions 2 and 3. A significant finding was that reaction rates were sensitive to the presence of certain hydrogen donors.



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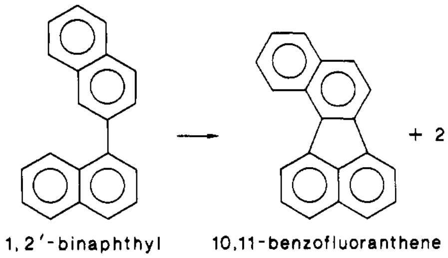

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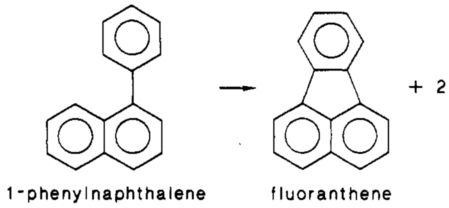

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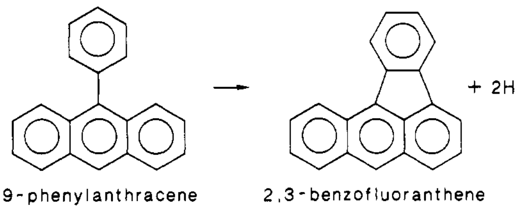

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Experimental Section

Reactions were done in sealed, evacuated Pyrex tubes (4 mm i.d. × 8 cm length) containing 20–40 mg of the reactant mixture. A Pyrex rod was inserted into each tube prior to sealing in order to minimize vapor volume. Vapor space accounted for less than 20% of the total volume. Pyrolysis was done by immersing tubes in a fluidized bath of iron oxide particles. Temperatures varied less than ±1.5 °C during an experiment.

Product mixtures were dissolved in dichloromethane and analyzed by capillary gas chromatography with flame-ionization detection. Fused silica columns with cross-linked methylsilicone coatings were used with elution temperatures up to 300 °C. Peak areas computed by the gas chromatographic system (HP Model 5880[6]) were converted to relative concentrations. Since peak areas did not precisely reflect relative concentrations (per C atom),

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(1) See, for example: *Proceedings of the Eleventh Symposium on Polynuclear Aromatic Hydrocarbons*; Battelle Laboratories: Columbus, OH, 1987.

(2) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(3) Hanch, C. *Chem. Rev.* **1953**, *53*, 353.

(4) Hurd, C. D. *The Pyrolysis of Carbon Compounds*; ACS Monograph 50; American Chemical Society: Washington, DC, 1929.

(5) (a) Kline, E. A.; Harrison, M. E.; Farnum, B. W. *Prepr.-Am. Chem. Soc., Div. Pet. Chem.* **1982**, *27*(3, 4), 18.

(6) Certain commercial materials and equipment are identified in this paper in order to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards nor does it imply the material or equipment identified is necessarily the best available for the purpose.

response factors were measured with calibration mixtures containing, when available, the compounds of interest. All major peaks were identified by coinjection and mass spectrometry. The primary analytical difficulty was a substantial decline in the instrument response factor for certain high molecular weight species (perylene, for example) when deposits built up in the inlet region. Frequent cleaning of the inlet was therefore necessary to obtain reproducible results.

Most compounds were obtained from commercial sources and were generally recrystallized before use. Purities measured by gas chromatography were greater than 99%. Since most experiments were done in the presence of radical scavengers (H donors), adventitious sources of free radicals are expected to have little effect.

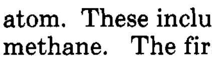
9,9′-Dixanthenyl was prepared by thermolyzing a free-radical initiator, di-*tert*-butyl peroxide, at 120 °C for 1 h in a benzene solution of xanthene.

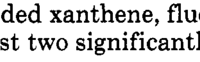
Results

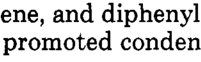
Preliminary Studies. Initial studies of 1,1′-binaphthyl condensation (reaction 2) were done at 440 °C in the presence of tetralin, 9,10-dihydrophenanthrene, and 9,10-dihydroanthracene. Findings were in agreement with those of Farnum et al.[5] Tetralin was essentially inert. In dihydroaromatic donors, extensive reaction occurred after about 15 min, generating a complex mixture of hydrogenated 1,1′-binaphthyls, naphthalene, 1,2,3,4-tetrahydronaphthalene, and both reduced and oxidized donors. Biaryl dissociation products represented an increasing fraction of the products with increasing reaction time, suggesting that dissociation occurred primarily via hydroaromatic intermediates. With decreasing concentrations of donors, relative concentrations of perylene increased and product distributions became less complex. Reactions in 9,10-dihydroanthracene/anthracene mixtures below 10% 9,10-dihydroanthracene generated relatively simple product mixtures. Here the only major hydrogenated product was 1,2,3,4-tetrahydroanthracene. Over a wide range of 9,10-dihydroanthracene concentration (2–90%), perylene formation was first order in *initial* donor concentration and reaction time, with an overall second-order rate constant of $10^{-5.1}$ M^{-1} s^{-1} (440 °C). A complex mechanism however must underlie this simple behavior since concentrations of 9,10-dihydroanthracene changed substantially during the reactions.

Very little condensation but extensive hydropyrolysis occurred in 9,,10-dihydrophenanthrene.

To avoid complex H-donation chemistry, detailed studies used donors capable of transferring just one H atom. These included xanthene, fluorene, and diphenylmethane. The first two significantly promoted condensation with the most active, xanthene, being roughly as effective as 9,10-dihydroanthracene. Diphenylmethane was relatively ineffective. Reactions of 1,1′-binaphthyl were the most thoroughly studied (reaction 2). Other biaryls examined were 1,2′-binaphthyl (reaction 3), 1-phenylnaphthalene (reaction 4), and 9-phenylanthracene (reaction 5). *p*-Terphenyl was used throughout as a diluent.


xanthene


fluorene


diphenylmethane

Decomposition of Donors and Diluent. At the temperatures of the present studies, all of the diluent/donor mixtures generated measurable pyrolysis products. Results of a series of cursory studies of these background reactions are summarized below.

Xanthene was the most thermally unstable of the donors, with a half-life of 100 min as a neat liquid at 440 °C (determined with biphenyl as an external standard). The major observed low molecular weight products were *o*-hydroxydiphenylmethane and its dissociation products, *o*-cresol and phenol. A number of high molecular weight products were formed, including several dixanthenyls and an unidentified peak with a parent mass corresponding to that of a dixanthene dimer that had lost H_2O (m/e 346). Trace amounts (of the order of 0.001 M) of 9,9′-dixanthenyl were observed. Formation of the major dixanthenyls was roughly second order in xanthene concentration, but relative amounts of the different isomers depended on reaction time and xanthene concentration.

Fluorene and diphenylmethane did not undergo extensive reaction under the conditions of the present studies. Diphenylmethane was the principal low molecular weight product of fluorene (5% after 1 h at 480 °C) and fluorene was the major product of diphenylmethane (1% after 1 h at 480 °C). As in the case of xanthene, thermally stable coupled products of these donors were the major high molecular weight products. Of particular interest in these studies were the concentrations of 9,9′-bifluorene and 1,1,2,2-tetraphenylethane, the dimers of radicals expected to predominate.

Concentrations of 9,9′-bifluorene in fluorene-containing systems were easily measured. They were (1) independent of reaction time; (2) nearly second order in fluorene concentration; (3) independent of the biaryls; (4) raised by a factor of 2 upon addition of 5% anthracene (at 440 °C, 90 min), a free-radical generator;[7] (5) reduced by a factor of 4–8 upon addition of free-radical traps (tetralin and 9,10-dihydrophenanthrene). In fluorene/*p*-terphenyl mixtures, at steady state, 9,9′-bifluorenyl concentrations were approximately proportional to the square of fluorene concentration and at 440 °C, [9,9′-bifluorenyl]/[fluorene] = 0.004.

In diphenylmethane systems, on the other hand, under all conditions concentrations of 1,1,2,2-tetraphenylethane were too small to be reliably detected ($\leq 10^{-4}$ M). The reason for these very low concentrations relative to 9,9′-bifluorenyl in fluorene may be connected with the greater thermodynamic stability (hence, possibly higher steady-state concentrations) of fluorenyl radicals than diphenylmethyl radicals.[8] Note that concentrations of radical recombination products depend on the square of the radical concentrations.

Dissociation of the diluent, *p*-terphenyl, was monitored by the formation of biphenyl. This reaction was very slow at the temperatures of the present experiments (typically 0.05% after 1 h at 480 °C). The presence of small amounts of each donor (1–2% w/w) increased biphenyl formation rates by a factor of ca. 2, while a further increase in donor concentration had little effect.

1,1′-Binaphthyl. Rates of product formation for reactions in xanthene at 440 °C are given in Table IA, reaction orders in Table II, and products at 440 °C as a function of xanthene concentration in Figure 1. Perylene was the major product. Its formation was first order in both 1,1′-binaphthyl (1–10% by weight) and xanthene (2–90%), with $k_2/M^{-1}\ s^{-1} = 7.2 \times 10^{-6}$. Over the range 360–560 °C

$$k_2/M^{-1}\ s^{-1} = 10^{5.9\pm0.6} \exp(-36.0 \pm 2.0\ \mathrm{kcal}/RT)$$

Other products of 1,1′-binaphthyl were 1,2′-binaphthyl, 10,11-benzofluoranthene, and naphthalene. Formation of

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[7] Billmers, R.; Griffith, L. L.; Stein, S. E. *J. Phys. Chem.* **1986**, *90*, 517.

[8] Manka, M. J.; Brown, R. L.; Stein, S. E. *Int. J. Chem. Kinet.* **1987**, *19*, 943.

Table I. Formal Second-Order Rate Constants for Reactions of Diaryls at 440 °C[a]

reactant	$k/10^{-6}$ M^{-1} s^{-1}				
	major condensation	dissociation	major isomerization	minor isomerization	minor condensation
		A. In Xanthene			
1,1'-BN	7.20 (Pery)	0.75 (Np)	0.79 (1,2'-BN)		0.29 (10,11-BF)
1,2'-BN	2.77 (10,11-BF)	0.95 (Np)	1.56 (2,2'-BN)	0.28 (1,1'BN)	
2,2'-BN		0.32 (Np)	0.77 (1,2'-BN)		
1-PhNp	0.21 (Fluo)	0.75 (Np)	0.80 (2-PhNp)		
9-PhAn	4.36 (2,3-BF)	11.4 (An)			
1-MeNp		5.74 (Np)			
2-MeNp		1.13 (Np)			
		B. In Fluorene			
1,1'-BN	1.35 (Pery)	0.38 (Np)	0.11 (1,2'-BN)		
1,2'-BN	0.46 (10,11-BF)	0.48 (Np)	0.29 (2,2'-BN)		
1-PhNp	0.09 (Fluo)	0.23 (Np)	0.12 (2-PhNp)		
1-MeNp		1.06 (Np)			
2-MeNp		0.24 (Np)			

[a] In all reactions, the weight percent diaryls was 5–10% and donor was 80–90%. Extents of conversion of diaryl were independent of diaryl concentration over this range. Each value was based on at least two runs, with reaction times varying from 30 to 90 min. These values are not true rate constants since the reaction order with respect to donor was often less than one (see Table II). However there was no noticeable variation in formal rate constant with extent of reaction. Products, given in parentheses, and reactants are as follows: BN, binaphthyl; 1-PhNp, 1-phenylnaphthalene; 9-PhAn, 9-phenylanthracene; MeNp, methylnaphthalene; Pery, perylene; Np, naphthalene; BF, benzofluoranthene; Fluo, fluoranthene; PhNp, phenylnaphthalene; and An, anthracene.

Table II. Kinetics Orders[a] **with Respect to Donor for Product Formation at 440 °C**[b]

reaction	condensation	dissociation	isomerization
Xn/1,1'-BN	1.09 (Pery)	0.58 (Np)	1.02 (1,2'-BN)
Fl/1,1'-BN	0.89 (Pery)	0.62 (Np)	0.73 (1,2'-BN)
Xn/1,2'-BN	1.11 (BF)	0.55 (Np)	1.10 (2,2'-BN)
Fl/1,2'-BN	0.74 (BF)	0.59 (Np)	0.75 (2,2'-BN)

[a] Uncertainties are generally less than 10%. Based on slopes of plots as shown in Figures 1 and 2. [b] BN, binaphthyl; Pery, perylene; Fl, fluorene; Xn, xanthene; and BF, benzofluoranthene.

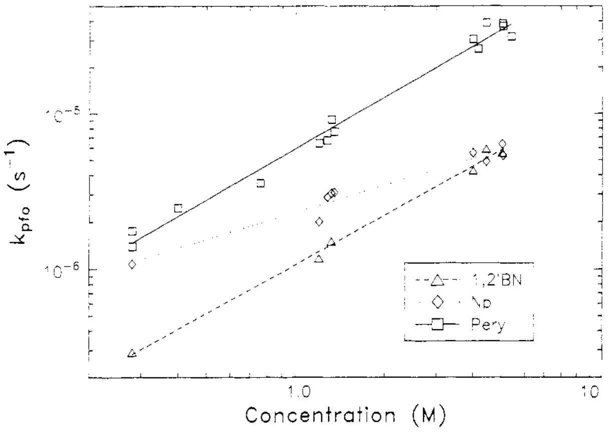

Figure 1. Log–log plots of pseudo-first-order rate constants, k_{PFO}, versus xanthene concentration for products from 1,1'-BN pyrolysis at 440 °C. $k_{PFO} = t^{-1} \ln \{[\text{product}]/[1,1'\text{-BN}]_{\text{initial}}\}$.

the first two of these was also first order in xanthene, but 8 and 22 times slower than perylene formation. The relative rate of naphthalene formation, on the other hand, was 0.6 order in xanthene, varying from a factor of 2 slower than perylene at 5% xanthene to 10 times slower at 90% xanthene. Naphthalene formation had an activation energy 10–20 kcal/mol higher than condensation.

Product formation rates for reactions in fluorene at 440 °C are given in Table IB. Products of 1,1'-binaphthyl are shown as a function of fluorene concentration in Figure 2. A product distribution similar to that in the reaction with xanthene was observed, but perylene formation was a factor of 6 slower and rates of naphthalene formation a factor of 2 slower. As shown in Table II, the reaction order with respect to fluorene was noticeably less than first order for all reactions.

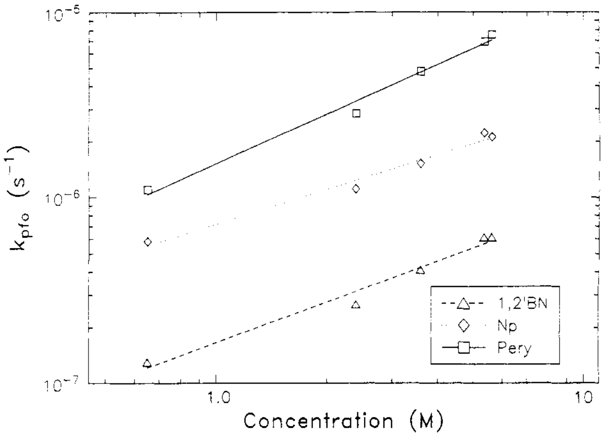

Figure 2. Log–log plots of pseudo-first-order rate constants, k_{PFO}, versus fluorene concentration for products from 1,1'-BN pyrolysis at 440 °C. $k_{PFO} = t^{-1} \ln \{[\text{product}]/[1,1'\text{-BN}]_{\text{initial}}\}$.

Because of its low rate of reaction at 440 °C, condensation by diphenylmethane has to be studied at higher temperatures. In 90% diphenylmethane at 480 °C, perylene formation was a factor of 60 slower than in xanthene at this temperature, but naphthalene formation was only about 4 times slower. The reaction order for all reactions in diphenylmethane was very low (<0.2).

Effects of several additives to both xanthene- and fluorene-containing mixtures were examined at 440 °C. Anthracene was added to increase radical concentrations.[7] It acted simply as a diluent. 2,2'-Binaphthyl was added to determine if the presence of naphthalene units influenced reaction rates. They did not. Tetralin and 9,10-dihydrophenanthrene were added to suppress concentrations of radicals and high molecular weight products of the donors. Their presence tended to increase rates of all reactions. For tetralin the rate increase for condensation was modest, reaching a maximum of 20–30% at 10% added tetralin.

The effect of added 9,10-dihydrophenanthrene was more complex. It was examined most thoroughly at 440 °C in 8:1 fluorene/1,1'-binaphthyl mixtures containing 10% 9,10-dihydrophenanthrene. At extents of conversion to perylene below 2% (<30 min), the presence of this donor both enhanced perylene formation rates by 20–30%, and led to the formation of an unidentified major product peak whose mass was four higher than a binaphthyl (*m/e* 258), but whose retention time suggested that it was a more condensed compound (it eluted well after 1,1′-binaphthyl and before perylene). At these low reaction extents, this species was present at concentrations approximately equal to that of perylene. At higher reaction extents (>90 min), the rate of perylene formation increased with a corresponding decline in the observed formation rate of this reduced species, indicating that it was a reaction intermediate.

1,2′-Binaphthyl. These reactions were studied in both xanthene and fluorene at 440 °C. Condensation occurred ca. 40% as fast as for 1,1′-binaphthyl. However, only one of the two possible condensation products could be identified (10,11-benzofluoranthene). Isomerization to 1,1′-binaphthyl and 2,2′-binaphthyl were one-tenth and two-thirds as fast, respectively, as condensation. Relative rates for reaction with fluorene and xanthene were nearly the same as found for 1,1′-binaphthyl.

1-Phenylnaphthalene. At 440 °C in xanthene, condensation to fluoranthene occurred $^1/_{30}$ as fast as 1,1′-binaphthyl formed perylene. Rearrangement to 2-phenylnaphthalene occurred at nearly the same rate as the rearrangement of 1,1′-binaphthyl to 1,2′-binaphthyl. In xanthene, rearrangement was 50% faster than dissociation, while in fluorene rearrangement was only one-half as fast as dissociation.

For the long reaction times required for these studies, products of donor decomposition began to interfere with product analysis. A reliable reaction order could therefore not be obtained.

9-Phenylanthracene. In undiluted xanthene and fluorene, this substance condensed to 2,3-benzofluoranthene at nearly the same rate as 1,1′-binaphthyl formed perylene. No isomerization products could be observed. Dissociation occurred about 3 times faster than condensation. The observed kinetic behavior was complex with the extent of reaction depending on the concentration of 9-phenylanthracene.

Other Reactions. To assist in the interpretation of results of the above experiments, the isomerization of 2,2′-binaphthyl to 1,2′-binaphthyl and the dissociation of 1- and 2-methylnaphthalene were examined in xanthene at 440 °C (Table I). In addition, studies of 1- and 2-fluoronaphthalene showed no isomerization products even under the most extreme conditions of the present experiments.

H/D Scrambling Studies. Mixtures containing 10% naphthalene-d_8 were heated in the presence of xanthene, fluorene, and diphenylmethane. Rates of H/D scrambling in the naphthalene were measured. In order to minimize systematic errors, relative rates were derived from relative reaction times necessary to achieve a given degree of H/D exchange ($\approx$20% naphthalene-d_7) as measured by the mass spectrum of naphthalene after reaction. Results are given in Table III. At 440 °C, rates were first order in donor concentration while at 360 °C, a noticeably higher reaction order (ca. 1.5) was followed.

Relative H/D scrambling rates for the different donors were in the same order as their effectiveness as condensation catalysts. In xanthene, fluorene, and diphenylmethane at 440 °C, relative scrambling rates were 40:13:1. Under the same conditions, relative condensation rates were 60:5:1 and absolute rates were a factor of 10–20 slower.

Discussion

Overview. All condensation reactions studied were markedly catalyzed by hydrogen donors containing a weak C–H bond (see Table IV). This behavior is peculiar in that reducing agents (donors) actually promoted oxidation (condensation).

Table III. Formal Second-Order Rate Constants for H/D Scrambling of Naphthalene-d_8 ($C_{10}D_8$) at 440 °C

H donor	% H donor	% $C_{10}D_8$	% *p*-terphenyl	$k/10^{-5}$ M^{-1} s^{-1} [a]
xanthene	94.0	6.0	0.0	7.25 (a)
xanthene	19.6	6.6	73.8	6.71 (b)
fluorene	92.5	7.5	0.0	0.54 (c)
diphenylmethane	92.4	7.6	0.0	0.19 (d)

[a] Corresponds to percent NpD_7H formed: (a) 10.8% in 5 min, (b) 16.7% in 40 min, (c) 20.0% in 120 min, and (d) 21.7% in 45 min.

Table IV. Benzylic C–H Bond Strengths (kcal/mol)

H donor	relative bond dissociation energy[a]
tetralin	(0)
9,10-dihydrophenanthrene	−1.5[b]
diphenylmethane	−4.5[c]
fluorene	−7.5[d]
9,10-dihydroanthracene	−10[e]
xanthene	−11[f]

[a] These energy differences are, in essence, equivalent to differences in Gibbs energies. [b] Estimated by Structure–Resonance Theory.[12] [c] Robaugh, D. A.; Stein, S. E. *J. Am. Chem. Soc.* **1986**, *108*, 3224. [d] From Gibbs energy measurements relative to the benzylic diphenylmethane C–H bond.[8] [e] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. Two different absolute values exist for this bond strength, one given in this reference, 75.2 ± 1.5 and the other 78.4 ● 1.8.[7] We prefer the latter since it was derived independently and the former was, in effect, based on a set of systematically "low" bond strengths (Tsang, W. *J. Am. Chem. Soc.* **1986**, *107*, 2872). [f] Estimated from relative abstraction rate constants (Russell, G. A. In *Free Radicals*; Kochi, J., Ed.; Wiley-Interscience: New York, 1973; Vol. I, p 275).

Both isomerization and dissociation occurred in competition with condensation, although the latter showed markedly different kinetic behavior (rates of dissociation were less sensitive to the nature and concentration of donor). As reaction conditions became more severe, the dependence of all reactions on donor concentration weakened and dissociation became increasingly significant.

We now analyze the mechanism in more detail. This analysis leads us to propose that the first step in all observed reactions is the transfer of a hydrogen atom to the reactant biaryl molecule. Hydrogen-transfer mechanisms are therefore examined first. Then, we examine the subsequent parallel processes of condensation, isomerization, and dissociation. We do not attempt to explain every observation made in the discussion section. Instead, we focus on findings that we feel are the most significant. Uncertainties in the thermodynamics of plausible intermediates were major obstacles to a more detailed analysis. Reasons for not choosing a conceptually simpler mechanism involving aryl radicals are given later.

Most of the following discussion focuses on reactions involving naphthalene moieties. Since H transfer to the anthryl moiety in 9-phenylanthracene is much faster[7] and the reaction followed more complex kinetics, it is discussed separately.

Hydrogen Transfer. In the presence of high concentrations of xanthene and fluorene, the direct transfer of an H atom from the donor to the reactant biaryl molecule is proposed as the predominant means of H transfer. For reactions leading to condensation of naphthyl-containing biaryls, we propose that hydrogen must first be transferred to the 7-position (the reason for choosing this particular position will be discussed later):

$$1,1'\text{-BN} + \text{D–H} \rightarrow (1,1'\text{-}\dot{\text{B}}\text{N–H}) + \dot{\text{D}} \qquad (6)$$

A related H-transfer process controls overall hydrogen migration in anthracene/9,10-dihydroanthracene systems.[7] Such reactions are simply the reverse of radical–radical disproportionation reactions and have been proposed as a ubiquitous means of radical formation in condensed phase pyrolysis chemistry.[9-11]

The proposed direct H-transfer reaction is consistent with both the observed first-order dependence of condensation on xanthene concentration and the strong dependence on donor C–H bond strength (the activation energy for this process is, in effect, equal to its reaction endothermicity, which is directly related to this bond strength). Moreover, an order of magnitude estimate for the rate of this reaction indicates that it has the potential of being fast enough to account for the observed reactions. This estimate is made with use of a published rate expression for H transfer from 9,10-dihydroanthracene to an anthracene structure[7] with corrections for reaction endothermicities (reaction 6 is 14 ± 3 kcal/mol more endothermic[12]) and reverse rate constants (the reverse of reaction 6 is estimated to be at least a factor of 5 faster[13]). The resulting rate expression ($10^{9.3\pm0.5}$ exp(−48.5 ± 3 kcal/RT) M^{-1} s^{-1}) yields a rate about 2 times slower than the observed rate of condensation. We estimate a factor of ca. 10 uncertainty in this estimate.

The direct H-transfer path, however, cannot account for all observed reactions. In the case of *p*-terphenyl dissociation, for example, this reaction is too slow to account for observed rates. This may be demonstrated as follows. Direct H transfer by donor molecules to a phenyl ring in *p*-terphenyl is approximately 10 kcal/mol more endothermic than transfer to a naphthalene unit.[12] Therefore, if both 1,1′-binaphthyl and *p*-terphenyl dissociation had resulted primarily from direct H donation, then at 440 °C the rate of 1,1′-binaphthyl dissociation would be approximately exp(10 kcal/RT) = 1000 times as fast as *p*-terphenyl dissociation. But under some conditions these processes only differed by a factor of 2 and in no case did they differ by more than a factor of 50. Other convincing evidence for the involvement of other means of H transfer is the observation that rates of *p*-terphenyl breakup were only slightly sensitive to the nature or concentration of the H donor. A different and unselective H-donation path must therefore be operative that depends little on the presence of H donors.

For this unselective path we propose that the key intermediates are free H atoms. These highly reactive intermediates might be expected to follow a low reaction order since they can be both formed and destroyed by donor molecules, as illustrated below:

$$\text{D–H} \rightarrow \dot{\text{D}} + \dot{\text{H}} \qquad (7)$$

$$\dot{\text{H}} + \text{D–H} \rightarrow \dot{\text{D}} + \text{H}_2 \qquad (8)$$

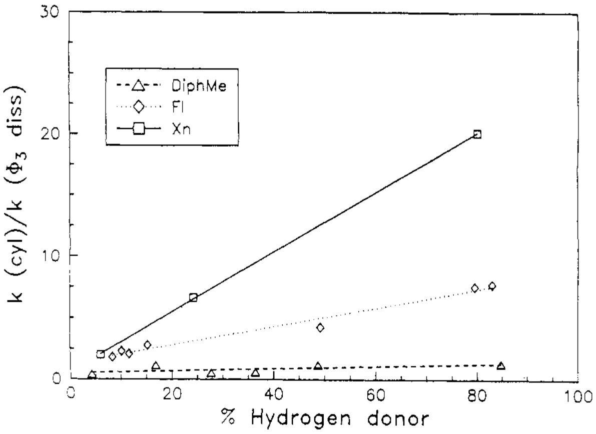

Figure 3. Relative rates of 1,1′-BN condensation and *p*-terphenyl dissociation as a function of concentration of xanthene (Xn), fluorene (Fl), and diphenylmethane (DiPhMe).

Another H-transfer process, involving H-atom migration from a "carrier" radical to an acceptor molecule, has been proposed as general means of hydrogen migration by McMillen and co-workers.[14] It has also been proposed as a key step in the H-donation chemistry of 9,10-dihydrophenanthrene.[15] In most of the present chemical systems, however, we believe that these processes are not significant. This reaction cannot explain how hydrogen is lost by single H-atom donors; it could only affect the migration of H atoms already removed from the donor. Moreover, the single H-atom donors used in the present studies are poor H-atom "carriers" due to their relatively low H-atom affinities. Consequently, these "carriers" are expected to dissociate far more readily than they can donate H atoms. On the other hand, H transfer by "carrier" molecules may be significant in reactions of hydroaromatic molecules, since radicals formed by H abstraction from these species have a donatable H atom.

Since *p*-terphenyl dissociation must result from nonselective H transfer, we use the observed formation rates of biphenyl from *p*-terphenyl as a general, semiquantitative measure of this process.[16]

Rate ratios of 1,1′-binaphthyl condensation versus *p*-terphenyl dissociation are shown in Figure 3 for the three donors used. These ratios provide a measure of relative rates for the selective and unselective H-transfer processes. Relative rates in the absence of the donor (i.e., the *y* intercept) give the relative rates for condensation and *p*-terphenyl dissociation via the unselective reaction. At high donor concentrations, contributions of the nonselective path to condensation are 3% for xanthene, 10% for fluorene, and >50% for diphenylmethane.

By subtracting the small contributions to perylene formation from the unselective path (based on measured amounts of biphenyl from *p*-terphenyl), rates can be estimated for reaction via the selective H-donation path. The correlation led to the following expression for condensation by xanthene through the selective H-donation path:

$$k_s/\text{M}^{-1}\ \text{s}^{-1} = 10^{5.6\pm0.7} \exp(-35.1 \pm 2.3\ \text{kcal}/RT) \qquad (9)$$

The comparable abilities of the three donors to cause dissociation of *p*-terphenyl (i.e., to generate a given concentration of H atoms) is consistent with the idea pres-

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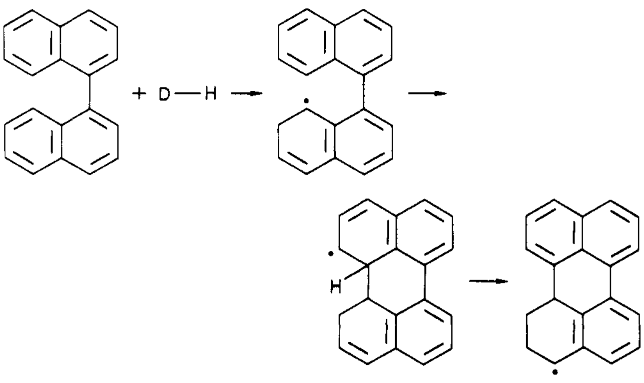
(16) Since all dissociation of *p*-terphenyl need not generate biphenyl, formation of biphenyl is not an exact measure of this reaction. Dissociation leading to biphenyl radicals that are not converted to biphenyl molecules would not be accounted for. This could cause measured rates to be up to a factor 2 slower than the actual rate of *p*-terphenyl breakup.

ented above that a more effective H-atom generator is also a better H-atom scavenger (see reactions 7 and 8). The initial source of labile hydrogen in neat *p*-terphenyl is unclear, but a very slow direct coupling reaction of *p*-terphenyl molecules, as observed in the pyrolysis of anthracene, is a possibility.[17]

We now consider H transfer to 9-phenylanthracene. Transfer to the anthracene unit is expected to be several orders of magnitude faster than to any of the other biaryls studied.[12] The relative stability of H atom/9-phenylanthracene adducts however means that they will dissociate slowly and are therefore more likely to be involved in bimolecular reactions. This, presumably, is the underlying cause of the more complex kinetics observed for reactions of 9-phenylanthracene.

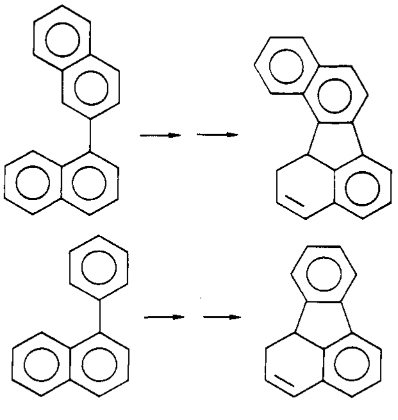
Condensation. We could not find a thoroughly convincing detailed mechanism for the condensation of H/biaryl adducts. After considering a number of alternative mechanisms for 1,1′-binaphthyl condensation, we chose the following as the least unsatisfactory:



I

The key reason for choosing this path was that it was only one providing a straightforward, thermodynamically accessible route leading to a stable precursor of perylene. The other paths led to relatively unstable cyclized species for which extensive hydrogen migration would be required to reach perylene. Rate estimates indicated that these other precursors would generally revert to starting materials.

While the isomerization step in this mechanism is unusual, it is driven by an estimated exothermicity of 15–20 kcal/mol. We consider the alternative path involving direct loss of an H atom as less likely largely because it appears to be inconsistent with observed relative rates of condensation. It would imply that relative rates should be sensitive to stabilities of the initially formed dihydrodiaryl condensation products. Hence, condensation rates of 1,2′-BN and 1-phenylnaphthalene would be very similar, since both reactions involve very similar initial products:



But the latter reaction was much slower than the former. Also, the relatively modest observed difference in condensation rates of 1,1′-BN and 1,2′-BN, despite the likely significant differences in endothermicities due to differences in strain in the condensed products, seem inconsistent with this path. On the other hand, since there is little precedent for the proposed isomerization step, we are by no means confident that it occurs in all (or any) reactions. The simplicity of the direct H-loss step along with the possibility that our thermochemical estimates are wrong indicate that the simple H-loss step should be considered as a plausible alternative. The α-tetrahydroperylene radical (I) formed by isomerization would be expected to be rapidly oxidized to perylene under most of the present experimental conditions.

The finding that H/D scrambling in naphthalene is 1 order of magnitude faster than condensation of 1,1′-binaphthyl is consistent with the proposed mechanism. The observed rate of scrambling is primarily a measure of the rate of H transfer to the 1-position in naphthalene, since transfer to the 2-position is expected to be significantly slower. Assuming that relative rates of H/D scrambling at the 1- and 2-positions of naphthalene are equal to the measured relative rates of methyl displacement at these positions, we estimate that scrambling at the 2-position is of the same order as the observed rate of condensation. This is consistent with the rough rate estimate given earlier for direct H transfer. It implies that a significant fraction of the H-atom additions to the 7-position in 1,1′-binaphthyl lead to condensation. The same ideas apply to 1,2′-binaphthyl condensation, but not to 1-phenylnaphthalene condensation. In the latter case the cyclization/H-transfer sequence is so slow that a substantial fraction (>90%) of the precursor H/1-phenylnaphthalene adducts lose an H atom before conversion to fluoranthene.

For the case of 9-phenylanthracene, addition of an H atom to the 2-position can lead to cyclization analogous to the above reactions. It occurs at a rate comparable to that for condensation of 1,1′-binaphthyl. The relative ease of forming the anthracene-derived radical[12] is apparently compensated for by the relative resistance of a phenyl ring toward condensation.

The experimental rate expression for condensation of 1,1′-binaphthyl in xanthene, even after correction for nonselective H transfer (expression 9), has significantly lower Arrhenius parameters than expected for simple H transfer. One possible explanation is that H loss from the H/1,1′-binaphthyl radical (reaction 10) is competitive with condensation, with the former process becoming increasingly significant with increasing temperature. Assuming,

$$\text{xanthene-H} + 1,1'\text{-BN} \rightarrow \text{xanthene}^{\bullet} + 1,1'\text{-BN-H}^{\bullet} \quad (10)$$

$$1,1'\text{-BN-H}^{\bullet} \rightarrow 1,1'\text{-BN} + \text{H}^{\bullet} \quad (11)$$

for instance, that H loss occurs by simple unimolecular C–H bond breaking (reaction 11), we derive a rate constant for condensation (k_{12}). If we make the assumption that

$$1,1'\text{-BN-H}^{\bullet} \rightarrow \text{“hydroperylene” radical} \quad (12)$$

H loss from the adduct (reaction 11) is competitive with condensation, then

$$k_s(\text{eq } 9) \approx \frac{k(\text{H add}) \times k(\text{cyclization})}{k(\text{H loss})} = k(\text{xanthene} + 1,1'\text{-BN} \rightarrow \text{xantheyl} + 1,1'\text{-BN-H}) \times k_{12}/k_{11}$$

After estimating that $k_{11} = 10^{14} \exp(-32 \text{ kcal}/RT) \text{ s}^{-1}$[18] and

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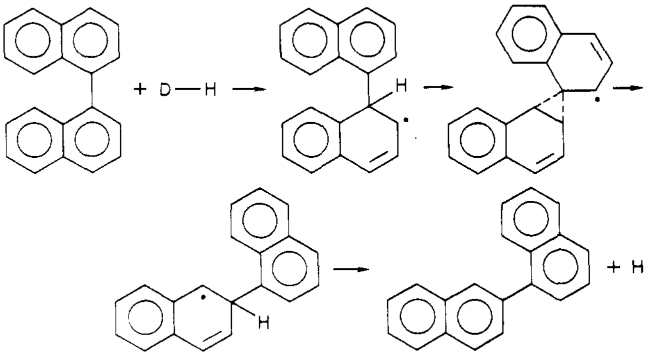
[17] Stein, S. E.; Griffith, L. L.; Chen, R. H. *J. Org. Chem.* **1987**, *52*, 1582.

using the xanthene donation rate constant given in the preceding section on H transfer, we derive the following effective first-order cyclization rate constant:

$$k_{12}/\mathrm{s}^{-1} = 10^{10.3\pm0.5} \exp(-19 \pm 5\ \mathrm{kcal}/RT)$$

This low A factor is consistent with a cyclic transition state in which the mobility in the H/1,1′-binaphthyl adduct has been lost.

Isomerization. Isomerization of the binaphthyls and 1-phenylnaphthalene followed the same kinetic behavior as condensation, suggesting that isomerization also involves H addition as a first step. The most straightforward mechanism is one in which an aryl substituent is transferred from one position to another via a "neophyl" rearrangement of the H/biaryl radical. This is illustrated below for the isomerization of 1,1′- to 1,2′-binaphthyl:



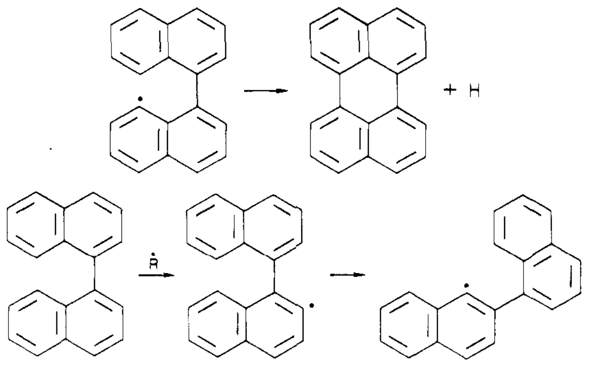
However, since this process involves the same intermediate radical as dissociation, it should follow the same kinetics. The noticeably stronger dependence of isomerization on donor concentration (Table II) suggests that there may be other, less obvious paths for isomerization.

Our failure to observe any isomerization of 1-fluoro- to 2-fluoronaphthalene or of 1-methyl- to 2-methylnaphthalene indicates that, in the observed aryl migrations, only the aryl substituents moved. The extrapolated rate for the unimolecular exchange of carbon atoms at the 1- and 2-positions of naphthalene[19] is far too slow to be observed under the present experimental conditions.

Dissociation. Products resulting from dissociation were observed in all reactions. Since the biaryl C–C bond is far too strong to undergo homolysis under the present conditions, and concentrations of polyhydrogenated species are very low, dissociation is presumed to occur by H-atom displacement of the aryl substituent.

Dissociation and condensation followed quite different kinetics. Dissociation had a lower reaction order and a greater temperature dependence and was less sensitive to the nature of the donor. Thus H transfer leading to dissociation is inherently less selective than transfer leading to condensation. According to the above discussion of H-transfer mechanisms, a large fraction of the H-transfer events leading to dissociation involve free H atoms than do the H-transfer events leading to condensation. This implies that H transfer to arylated positions by the direct H-transfer process is substantially slower than transfer to unsubstituted positions. The loss of resonance energy and perhaps steric impediments may account for the low rate of selective transfer. In further support of this idea, displacement of a 1-naphthyl substituent on naphthalene was approximately 10 times slower than displacement of a methyl substituent and 10 times slower (per position) than H/D scrambling of naphthalene.

Aryl Radical Mechanisms for Condensation. Certain qualitative aspects of the observed reactions are consistent with reactions involving aryl radical intermediates. As illustrated below, both condensation and isomerization could result from aryl precursors: The very small quantities of diaryls formed would imply that any aryl radicals formed that are incapable of unimolecular reaction simply abstract H atoms from the donors.



However, we have been unable to construct a plausible mechanism involving aryl radicals that even coarsely accounts for observed relative rates and kinetics. A key problem in these mechanisms results from the presumption that the ease of formation and reactivity of aryl radicals do not depend strongly on the specific radical site.[17,20,21] If this presumption were seriously in error, one might be able to construct complex, sometimes reversible reaction paths that could rationalize relative rate observations. However, even in this case, the observed high reaction order in xanthene and fluorene and the relative ease of forming high-energy aryl radicals would need to be explained. We therefore prefer the above H-addition mechanism.

Summary and Conclusions

The critical intermediates in all observed reactions of biaryls, including condensation, isomerization, and dissociation, are free radicals derived from the attachment of H atoms to the reactant biaryl molecules. At higher concentrations of the more active donors (xanthene and fluorene), the H-transfer process that leads to reaction is very sensitive to reaction thermochemistry. Kinetic observations and thermochemical arguments suggest that this path involves direct H transfer from the donor to the biaryl molecule. At low donor concentrations or in the presence of a poor donor (diphenylmethane), a nonselective H-transfer path dominates. We propose that this path involves free H atoms and that the observed nonintegral reaction orders with respect to donor are a consequence of varying contributions of the two H-transfer mechanisms.

Condensation of 1,1′-binaphthyl is proposed to be initiated by H transfer to a remote position (the 7-position). The adduct then undergoes intramolecular ring closing followed by irreversible H migration from the attacked carbon in one ring to a double bond in the other. Under most of the conditions of our experiments, the product tetrahydroperylenyl radical is then rapidly oxidized to

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(18) This is based on an estimate from ref 12 that H addition to the 2-position in naphthalene is 28 kcal mol^{-1} exothermic and has the same rate constant as addition to benzene ($10^{10.6} \exp(-4\ \mathrm{kcal}/RT)\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$: Kerr, J. A.; Parsonage, M. J. *Evaluated Kinetic Data on Gas Phase Addition Reactions*; Butterworths: London, 1972; p 49).

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perylene. Similar mechanisms are proposed for the other condensation reactions.

Aryl migration occurs in parallel with condensation. In this reaction only the aryl groups move. Methyl and fluoro substituents do not migrate under our experimental conditions.

Dissociation is generally less sensitive to the nature and concentration of the donor than is condensation or isomerization. This, it is suggested, is due to significantly lower rates of selective H transfer to the position leading to dissociation (arylated positions) than to positions leading to the other reactions (unsubstituted positions). As a result, lower order, nonselective H-transfer process tend to play a more important role in dissociative processes.

These studies clearly distinguish three regimes of hydrogen transfer. In the presence of reactive, multiple H-atom-donating species, hydropyrolysis predominates. In this environment, addition of an H atom to an aromatic ring initiates ring hydrogenation. In the presence of less effective donors, conditions that might be attained after reactive hydroaromatic molecules have been oxidized, selective means of H transfer predominate, leading to both condensation and dissociation. Rates of H transfer under these conditions depend strongly on the thermodynamics of H-atom transfer (that is, on the R–H bond strength of the donor and the hydrogen atom affinity of the acceptor). In the absence of donors containing labile H atoms, H transfer via free H atoms predominates. In this regime, H transfer is unselective and rates depend little on the nature of the donor.

Acknowledgment. This research was supported by a grant from the Gas Research Institute.

Registry No. 1,1′-Binaphthyl, 604-53-5; 1,2′-binaphthyl, 4325-74-0; 1-phenylnaphthalene, 605-02-7; 9-phenylanthracene, 602-55-1; xanthene, 92-83-1.

Chemistry of Dioxiranes. 10. Oxidation of Quadricyclane and Norbornadiene by Dimethyldioxirane[1]

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Treatment of quadricyclane (**2**) with dimethyldioxirane (**1**) leads to the formation of *exo*-norborna-2,5-diene monoepoxide (**4**), *exo*,*exo*-norborna-2,5-diene diepoxide (**5**), bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (**6**), and *exo*-2,3-epoxybicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde (**7**). The reaction is believed to involve prior catalyzed isomerization of **2** by **1** to norbornadiene (**3**) and subsequent conversion of **3** to the observed products. Under suitable conditions **1** reacts with **3** to give **4** and **6** in a 97:3 distribution, respectively.

Evidence for the intervention of dimethyldioxirane (**1**) in the reaction between monoperoxysulfuric acid and acetone has been reported by Edwards, Curci, and coworkers.[2] The case for the production of **1** in this reaction was made even more convincing by our demonstration[3] that **1** could be removed from the generation vessel and obtained as a solution in acetone. Indeed we have shown[3] that a number of methyldioxiranes can be prepared by a similar procedure. Acetone solutions of **1** have also been used to obtain a range of spectroscopic data on **1**.[3-5] The observation[4a] of a single peak in the ^{17}O NMR spectrum of **1** is particularly telling and clearly distinguishes **1** from the isomeric carbonyl oxide.

Dimethyldioxirane is a powerful O-atom donor. It has been shown to transfer an O atom rapidly and efficiently to olefins,[2,3] polycyclic aromatic hydrocarbons,[3,6,7] phosphines,[3] sulfides and sulfoxides,[1,3,5,8] imines,[9] and azo compounds.[9] In addition it inserts O atom into nitrogen–hydrogen[10] and carbon–hydrogen[11] bonds. In the latter case **1** demonstrates a unique chemistry that appears to resemble that of some monooxygenase enzymes.[12] In many respects the chemistry of **1** parallels that of some oxiziridines which Davis et al.[13] are studying, in part, because of their possible relationship to flavin-dependent monooxygenases.

Our continuing work on the chemistry of dioxiranes is proceeding along two lines. In one line of research we are carrying out physical organic studies designed to elucidate the details of the O atom transfer and insertion reactions. We are also attempting to demonstrate the synthetic

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