Preparation of Alkyl-Substituted Biphenylenes by the Pyrolytic Extrusion of Nitrogen from Benzo[c]cinnolines

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Flash vacuum pyrolysis of 1,10-dimethylbenzo[c]cinnoline (**1a**) at 730 °C (0.12 Torr) provides 1,5-dimethylbiphenylene (**6**) in 71% (53% isolated) yield, whereas pyrolysis of 1,10-diethylbenzo[c]cinnoline (**1b**) produces a complex mixture containing some 1,8-diethylbiphenylene (**8**) (11.3%) but more phenanthrene (**9**) (12.9%) as well as a myriad of other side products. The preparation of the benzo[c]cinnolines and an investigation of the mechanism of phenanthrene formation are described. A straightforward correspondence between the mass spectrum of **1b** and the pyrolysis pathway leading to phenanthrene is noted. The enhanced rates of side reactions in the pyrolysis of **1b** are rationalized by estimating activation barriers for the processes competing with N_2 extrusion and with ring closure.

Our interest in the structure, stability, and magnetic properties of π networks containing multiply fused ($4N$)- and ($4N + 2$)-membered rings has led to the synthesis of several annelated biphenylenes possessing an interesting mixture of aromatic, antiaromatic, and olefinic properties.[2] These hydrocarbons were typically synthesized by bis-Wittig cyclization of derivatives of 1,8-dimethylbiphenylene, a compound prepared in low to moderate yield by dimerization of 3-methylbenzyne.[3]

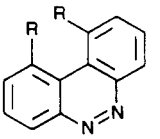
The dimerization procedure, although straightforward and rapid, suffers from a number of drawbacks. Foremost among these is the formation of a mixture of head-to-head and head-to-tail dimers. While these can be separated by spinning band ethylene glycol codistillation,[3a] the separation is time consuming and tedious, the net result being that the mixture was usually used directly in the next step in the hope that subsequent derivatives would permit convenient purification. Another drawback of the benzyne dimerization is the explosion hazard presented by the common diazotization route to benzyne.[3b] The alternate benzoaminotriazole route,[3c] while safe, involves a multistep synthesis, which limits the scale of the preparation.

Extension of our work to hydrocarbons of greater complexity required a source of 1,5-dialkylbiphenylenes in relatively large quantities and in isomerically pure form. Flash vacuum pyrolysis has become standard methodology for the synthesis of highly strained or thermodynamically unstable systems.[4] In particular, the pyrolytic extrusion of nitrogen from benzo[c]cinnolines has been established[5] as a practical method for the synthesis of biphenylenes. We have found that flash vacuum pyrolysis of 1,10-dimethylbenzo[c]cinnoline at 730 °C does indeed produce 1,5-dimethylbiphenylene in synthetically useful quantities (26% from 2-methylaniline, not including recovered intermediates). The details of our procedure are given in the Supplementary Material.

Our attempts to extend the benzocinnoline pyrolysis procedure to 1,8-diethylbiphenylene unexpectedly led to the formation of a complex mixture containing significant quantities of over 20 hydrocarbons. Although a major component of this mixture was the desired biphenylene (11% yield), phenanthrene was present in comparable quantity. This unexpected loss of C_2H_6 prompted a study of the mechanism of phenanthrene formation, which is described in this paper. Our results are discussed in terms of the estimated activation barriers for the competing processes in the pyrolysis. This analysis provides a rationale for the domination of the undesired pyrolysis products that accompanied the seemingly innocuous substitution of ethyl for methyl.

Results and Discussion

Synthesis of the Benzo[c]cinnolines. Although nitrogen extrusion from either 1,10- or 4,7-disubstituted benzocinnolines would lead to 1,8-dialkylbiphenylenes, we chose to study the 1,10-isomers (**1a,b**) because of MacBride's observation[5a] that bulky substituents in the 1,10-positions reduce pyrolysis temperatures, increase conversion percentages, and lead to higher yields of biphenylenic products. A further reason for studying the 1,10-di-



1a: R = CH_3
b: R = C_2H_5

alkylbenzocinnoline pyrolysis was that the dimethyl compound was a known material.[6]

Unfortunately, the published procedures for preparing the benzocinnoline and its precursors suffered from poor yields, scale limitations, and inconvenient procedures. We felt that a modified procedure could be developed that would overcome these difficulties. In the case of the dimethyl compound, this objective has been met; we have been able to prepare >100-g lots of 1,10-dimethylbenzo[c]cinnoline in less than a week.

(1) Based on the Ph.D. dissertation submitted by K.R.L. to the Cornell Graduate School, 1987.

(2) (a) Wilcox, C. F., Jr.; Blain, D. A.; Clardy, J.; Van Duyne, G.; Gleiter, R.; Eckert-Maksic, M. *J. Am. Chem. Soc.* **1986**, *108*, 7693–7702. (b) Wilcox, C. F., Jr.; Weber, K. A. *Tetrahedron* **1985**, *41*, 4425–4436. (c) Wilcox, C. F., Jr.; Farley, E. N. *J. Org. Chem.* **1985**, *50*, 351–356 and references therein.

(3) (a) Wilcox, C. F., Jr.; Uetrecht, G. D.; Grantham, G. D.; Grohman, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 1914–1920 and references therein. (b) Logullo, F. M.; Seitz, A. W.; Friedman, L. *Org. Synth.* **1968**, *48*, 12. (c) Campbell, C. D.; Rees, C. W. *J. Chem. Soc. C* **1969**, *5*, 742.

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In the first step of the preparation, 2-nitro-6-methylacetanilide (**2a**) was prepared[7a] in one pot by addition of the 2-methylaniline to acetic anhydride followed by treatment of the protected amine with HNO_3. The resulting mixture of 2- and 4-nitro-6-methylacetanilides was separated by use of the Witt–Utermann solution (KOH in ethanol/water), which dissolved **2a**; the insoluble, 4-nitro isomer was removed by filtration. Acidification of the filtrate with acetic acid gave 2-nitro-6-methylacetanilide in 55% yield. This material was of sufficient purity to be used directly in the next step. An analogous procedure was used to prepare 2-nitro-6-ethylacetanilide (**2b**).[7b,c] Although in this case pure compound was not obtained after the Witt-Utermann treatment, the mixture was enriched to the extent that analytically pure **2b** could be obtained by recrystallization.

The acetanilides were deprotected, diazotized, and converted to the 2-iodo-3-alkylnitrobenzenes (**3a,b**) in one operation. Hydrolysis to the aniline was accomplished by refluxing the acetanilides for several hours in concentrated HCl. The resulting free amines were not isolated, but the solutions were cooled and diazotized at once by addition of $NaNO_2$. The diazonium chlorides that formed were poured into ice-cold aqueous KI, and, after the vigorous evolution of nitrogen and iodine vapor had subsided, the iodine that had formed was reduced by addition of excess $NaHSO_3$. The products were isolated by filtration (**3a**, 92%) or extraction (**3b**, 67%).

Ullman coupling of **3a** and **3b** in refluxing DMF[8] produced 6,6′-dimethyl-2,2′-dinitrobiphenyl (**4a**, 86%) and the corresponding diethyl compound (**4b**, 55%) in good yields. The iodide, Cu powder, and dry DMF were refluxed for 4 h; another portion of Cu was added, and the mixture was refluxed for an additional 4 h. Failure to add the second portion of Cu resulted in incomplete conversion, presumably because fresh surface is required for the reaction to occur. The reaction also failed unless the DMF was carefuly dried before use. Workup was accomplished by separating the inorganic material from the reaction mixture by filtration, and pouring the filtrate into water. The precipitated product was collected and recrystallized to afford the biphenyls.

Reduction of **4a** and **4b** with $LiAlH_4$[9] in a mixture of Et_2O and benzene provided the benzocinnolines in 96% (**1a**) and 87% (**1b**) yields. The ratio of ether to benzene in the reaction medium appeared to be an important factor in determining the course of the reaction. If the reaction was done in pure Et_2O, overreduction to the diaminobiphenyl (approximately 25% by NMR integration) was observed. In contrast, if the reaction was done in pure benzene, the reaction mixture consisted largely of starting material even after prolonged periods. The optimum ratio of Et_2O to benzene was found to be 3:4. The product was isolated by decomposition of the excess $LiAlH_4$ by careful addition of H_2O and aqueous NaOH, separation of the supernate from the granular precipitate, and evaporation of the solvent from the filtrate. This material generally was spectroscopically homogeneous, and was used without further purification in preparative runs. In some instances, air was bubbled through the solution to complete the conversion of the hydrazo compound to the benzocinnoline. Analytical samples were obtained by sublimation (**1a**) or chromatography (**1b**).

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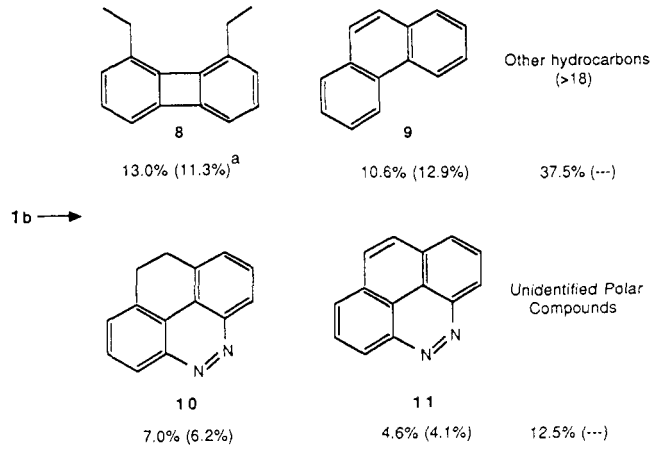
Scheme I



[a] Weight percent of crude pyrolysate (molar yield based on **1b** introduced).

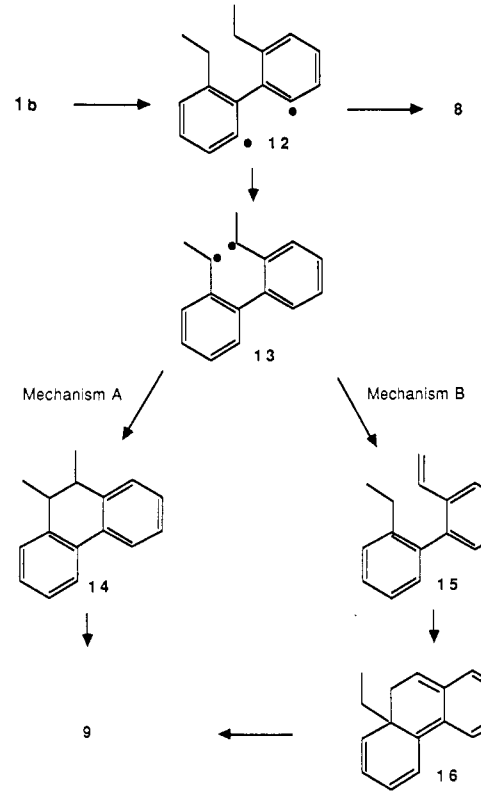
Pyrolysis of the Benzocinnolines. In preliminary, small-scale experiments, flash vacuum pyrolysis of **1a** at 734 ± 4 °C (0.6 Torr) produced dark, oily crystals in 86% mass balance. This crude pyrolysate was estimated to contain ca. 14% unreacted starting material (NMR integration). Gas chromatographic analysis of the hydrocarbon portion of the mixture showed that the primary components were 1,8-dimethylbiphenylene (**6**, 80%) and 9,10-dihydrophenanthrene (**7**, 13%). The yield of **6**, determined by GC, was 71% based on consumed **1a**.

The best results in preparative runs were obtained when no more than 5 g of starting material were used. In a typical experiment, several 5-g lots were pyrolyzed and the crude pyrolysates were combined. Ethylene glycol codistillation followed by recrystallization from MeOH afforded 1,8-dimethylbiphenylene in 53% isolated yield. The excellent yield coupled with the availability of large (>100 g) quantities of **1a** make this an attractive method for the preparation of 1,8-dimethylbiphenylene. Attempts to increase the scale of a pyrolysis to 100 g resulted in a marked decrease in yield. Since little starting material was recovered in these larger pyrolyses, the decrease in yield can probably be attributed to intermolecular reactions, which become competitive at higher reaction pressures, rather than to factors such as inefficient heat transfer.

Extension of this procedure to the prepartion of 1,8-diethylbiphenylene (**8**) proved to be disappointing. Flash vacuum pyrolysis of **1b** by use of the above conditions produced a 77% mass balance and a complex mixture of products (Scheme I). The complexity of this mixture and the low yield of **8** precluded the use of this method as a preparative procedure. However, the mere fact that the failure of the reaction was so unexpected motivated us to study it in more detail. We hoped to learn more about the factors controlling the product distribution in pyrolytic processes of this type and possibly use them to modify the course of the reaction.

Mechanism of Phenanthrene Formation. There are two plausible mechanisms for phenanthrene formation, which are depicted in Scheme II. The first (mechanism A) involves nitrogen extrusion to give **12**, hydrogen atom abstraction from the benzylic positions to form the biradical **13**, and ring closure to **14** followed by loss of two methyl radicals to give phenanthrene (**9**). This mechanism could also easily explain why substantial amounts of 9,10-dihydrophenanthrene were formed in the pyrolysis of **1a**. We initially objected to this mechanism on the grounds that if the loss of the methyl groups in the final

Scheme II

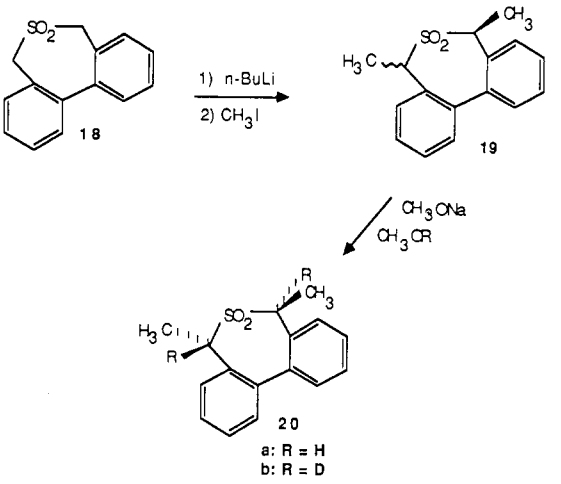


step were possible, dehydrogenation should be observed in the pyrolysis of **1a**. However, the bond dissociation energy for a methyl–benzyl bond is ca. 15 kcal/mol less than that for a hydrogen–benzyl bond.[10] At 1000 K, this represents a rate ratio of nearly 1900. Hence it is possible that dihydrophenanthrene would not be dehydrogenated under these conditions.

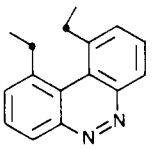
The alternative pathway (mechanism B) involves the same formation of **13**, but now **13** disproportionates to produce 2-ethyl-2′-vinylbiphenyl (**15**), which undergoes electrocyclic ring closure to form **16**. Elimination of ethyl and hydrogen radicals leads once again to phenanthrene. On the basis of thermochemical estimates of the relative exothermicities of the two steps leading from **13**, mechanism B is favored. Benson group additivity calculations[10] indicate that at 1000 K the free energy change upon formation of 2-ethyl-2′-vinylbiphenyl is ca. 16 kcal/mol more exothermic than ring closure to **14**. If the transition states reflect this "thermodynamic driving force" to the extent of even 25%, pathway B is favored by a substantial amount. The remaining steps of mechanism B are plausible as well. The rate of the pericyclic ring closure of **15** was estimated by applying the Wilcox–Carpenter model.[11] From the known activation parameters[12] for the ring closure of hexatriene, the halflife for cyclization of **15** was estimated to be on the order of milliseconds, a time considered to be much shorter than the contact time in the tube.

The mechanisms can, in principle, be distinguished by running the reaction with the labeled benzocinnoline **17**. Mechanism A would lead to formation of phenanthrene

Scheme III



labeled at both C9 and C10, while mechanism B would lead to phenanthrene labeled at C9 but not C10. However, since the two mechanism diverge at **13**, any precursor to labeled **13** will do as well. Because of the anticipated synthetic inaccessibility of **17**, we chose to generate labeled **13** by the pyrolysis of a labeled sulfone.



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Synthesis of the Biradical Precursor. The labeled biradical can be generated by extrusion of SO_2 from 5,7-dimethyl-5,7-dihydrodibenzo[c,e]thiepin 6,6-dioxide (**20**), the synthesis of which is outlined in Scheme III. Addition of *n*-BuLi to a THF solution of the sulfone **18**[13] led initially to a yellow solution, which upon addition of a second equivalent of base became orange. The resulting solution of 1,3-dilithiosulfone was quenched with CH_3I at −78 °C and warmed to 0 °C. Workup gave a quantitative yield of a mixture of cis and trans sulfones (cis:tris = 60:40, NMR integration). The preference for the cis isomer suggests dilithio bridging, reminiscent of that observed by Schleyer et al.[14] in several dilithio species. Such an interpretation is in conflict with the recent calculations of Streitwieser, which indicated that *trans*-dilithio dimethylsulfone is more stable.[15]

The NMR spectrum of this mixture is of some interest. It consists of, in addition to the aromatic multiplet centered at 7.48 ppm, a set of three quartets centered at 4.33, 4.21, and 3.99 ppm in the ratio of 20:20:60 and a set of three upfield doublets centered at 1.76, 1.75, and 0.93 ppm in the ratio 60:20:20. These results can be interpreted in terms of the lowest energy conformations of the isomers formed. The trans isomer, in which the methyl groups are chemically equivalent, adopts a conformation in which the methyl groups are in the plane of the aromatic rings, resulting in a relative downfield shift for these resonances (1.76 ppm). This conformation forces the benzylic protons over the plane of the rings, causing a slight upfield shift

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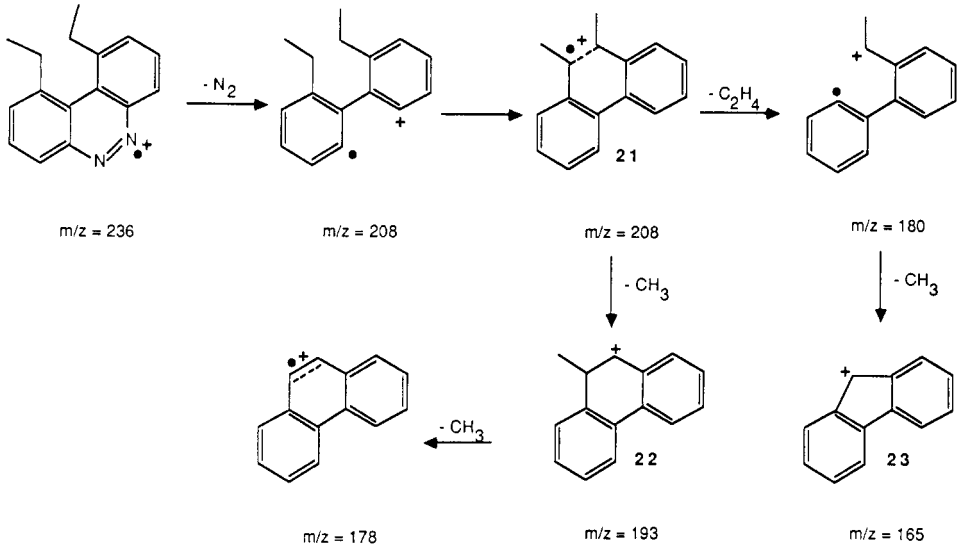
(14) For example see: (a) Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1982**, *228*, 107. (b) Neugebauer, W.; Clark, T.; Schleyer, P. v. R. *Chem. Ber.* **1983**, *116*, 3283.
(15) Bors, D. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 1397–1404.

Scheme IV



to 3.99 ppm. In the lowest energy conformation of the cis isomer, however, one of the methyl groups is forced over the top of one of the rings, resulting in a substantial upfield shift (to 0.93 ppm) relative to the methyl in the plane of the ring.

Epimerization to the more stable trans isomer was accomplished by refluxing the mixture in a solution of NaOEt in ethanol. Recrystallization provided the trans sulfone (**20a**) in 56% isolated yield. The labeled sulfone (**20b**) was prepared in a similar manner by refluxing the mixture in MeOD containing MeONa.

Pyrolysis of the Sulfone. When **20a** was subjected to the conditions used for pyrolysis of **1b**, phenanthrene (**9**) was a major product, in agreement with the hypothesis that biradical **13** is the intermediate leading to **9** in the benzocinnoline pyrolysis. A substantial amount of 9,10-dimethyl-9,10-dihydrophenanthrene (**14**) was also formed, providing evidence in favor of mechanism A. Further evidence was provided by performing the pyrolysis at 550 °C (0.2 Torr). This led cleanly to **14** (86% isolated yield), which, when subjected to the more extreme conditions (730 °C), gave **9**. Although these results clearly favor mechanism A, the possibility that **14** is not on the pathway to phenanthrene cannot be rigorously excluded; reversible ring closure followed by formation of ethylvinylbiphenyl (**15**) and the remaining steps of mechanism B is a plausible alternative.

That this hybrid mechanism is not operative was demonstrated by pyrolizing labeled sulfone (**20b**). Pyrolysis at 730 °C produced a mixture containing primarily 9,10-dihydro-9,10-dimethylphenanthrene-*9,10-d*$_2$ (62.6%) and phenanthrene-*9,10-d*$_2$ (29.0%). The formation of doubly labeled compounds was verified by GCMS. In order to exclude the possibility that double-labeled product was produced by scrambling prior to formation of ethylvinylbiphenyl,[16] ^{1}H, ^{2}H, and ^{13}C NMR spectra of the phenanthrene product were examined; these indicated that the ^{2}D labels were located exclusively on C9 and C10 (see the Experimental Section). In conclusion, the sulfone pyrolysis experiments favor mechanism A.

Correlation with Mass Spectral Fragmentation Patterns. Perhaps the formation of phenanthrene in the pyrolysis of **1b** should not have been surprising in view of the known empirical correlations between pyrolytic reaction pathways and mass spectral fragmentation patterns.[17] The mass spectrum of 1,10-diethylbenzocinnoline, in fact, exhibits its parent peak at *m/z* 178, the mass of phenanthrene! Examination of the mass spectrum reveals a straightforward correspondence between it and mechanism A (see Table I and Scheme IV). Ionization, loss of N_2, and H atom migration followed by formation of a one-electron bond between the benzylic carbon atoms gives **21**. Loss of methyl from **21** provides **22** (*m/z* 193) as a logical consequence of formation of the intermediate. Loss of a second methyl provides a peak at *m/z* 178. The peak at *m/z* 165 probably arises from a pathway parallel to that leading to phenanthrene since this peak is absent in the mass spectrum of phenanthrene. Although we can only speculate, it seems likely that this peak is due to fluorenyl cation (**23**) formed by loss of C_2H_4 from **21** followed by ring closure and loss of methyl.

It is worthwhile noting that the mass spectrum of the **20a** is very similar to that of **1b** for *m/z* less than 208, in agreement with the hypothesis that **13** is an intermediate in the fragmentation of the benzocinnoline. Additional support is provided by the mass spectrum of the dideuterated sulfone, **20b**.

Activation Barriers for Competing Processes. If one assumes that N_2 extrusion occurs in a stepwise fashion, that is by initial cleavage of a single aryl–nitrogen bond,[18]

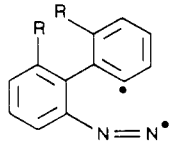
Table I. Mass Spectral Data for 5b, 20a, and 20b

compd	*m/z* (intensity)
5b	237 (17.34), 236 (73.67), 193 (43.92), 180 (10.70), 179 (54.43), 178 (100.0), 177 (10.57), 176 (11.65), 165 (33.92), 152 (12.34), 89 (10.63), 63 (10.82), 43 (11.71)
20a	272 (1.03), 208 (47.93), 194 (19.96), 193 (100.0), 179 (25.45), 178 (57.59), 165 (12.60)
20b	274 (0.55), 210 (41.79), 208 (11.00), 196 (15.51), 195 (100.0), 193 (10.01), 180 (52.53), 179 (11.81)

(16) Label scrambling has been observed in the mass spectrum of phenanthrene-*9,10-d*$_2$; MacDonald, C. G.; Shannon, J. S. *Aust. J. Chem.* **1962**, *15*, 771–85.

(17) Dougherty, R. C. *Top. Curr. Chem.* **1974**, *45*, 93.

a zeroth-order approximation for the activation energy of the process can be estimated as the difference in energy between the heat of formation of nitrogen-centered biradical **24** and the heat of formation of benzo[c]cinnoline.



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From Benson's group additivities,[10] the biradical has a heat of formation of 171.7 kcal/mol; the heat of formation of benzocinnoline has been measured[19a] to be 94.8 kcal/mol, leading to an estimated activation energy of 76.9 kcal/mol. Although this is probably somewhat of an overestimate due to neglect of the steric interactions between the alkyl groups in the starting material that alkyl–benzyl bond cleavage, which has a measured activation energy of 72.7 kcal/mol for ethylbenzene,[19b] is at least competitive with aryl–nitrogen bond homolysis.

This is in contrast to the results of a similar calculation for **1a**. In this cas, C–H bond homolysis has an activation enthalpy of 85 kcal/mol,[10] an amount well in excess of that required to break the C–N bond of the benzocinnoline (again approximated as 76.9 kcal/mol). It is not surprising, therefore, that azapyrenes **10** and **11** are not observed in the pyrolysis of **1a**.

Of those diethylbenzocinnoline molecules that form **12**, many are diverted to **13** because of the additional stabilization of the radical centers not available in the dimethyl case. Group additivity estimates of $\Delta\Delta G°$ at 1000 K indicate H atom abstraction to form the methyl-substituted benzyl radical is ca. 4.4 kcal/mol more exothermic than H atom abstraction at an unsubstituted site. To the extent that this energy difference is reflected in the transition state for the reaction, H atom abstraction will be favored in the case of formation of the alkyl centered radical. This quantity can be estimated by using the empirical correlation of Polanyi and Semenov,[20] which indicates that ca. 25% of the difference in exothermicity is reflected in the transition state for reactions of this type. This leads to an estimate that H atom abstraction is ca. 1.7 times faster in the diethyl case. This information combined with the observation that pyrolysis of **1a** produces 14% 9,10-dihydrophenanthrene indicates that even if N_2 extrusion occurred cleanly in the pyrolysis of **1b**, the product mixture would still contain ca. 25% products derived from benzylic hydrogen atom abstraction.

Conclusions

Two major branchpoints in the reaction pathway divert the reaction from formation of biphenylene to formation of side products. The first involves homolysis of the alkyl–benzyl bond in competition with aryl–nitrogen bond cleavage; the second involves the partitioning of **12** between ring closure to form **8** and abstraction of benzylic H atoms, which leads to various side products. The enhanced rate of reactions leading to side products in the pyrolysis of **1b** relative to **1a** can be rationalized from the estimated activation barriers for the competing processes.

The thermochemical analysis indicates that there are two problems arising from substituting ethyl for methyl on the benzocinnoline. The problem of benzylic H atom abstraction could be solved by using less stabilizing radical centers at the 1- and 10-positions, or, perhaps more elegantly, by tying the biradical back on itself by joining the 1- and 10-positions through a ring. Clearly, a simple alkyl ring will not do since alkyl–benzyl bond cleavage will again be a problem. However, joining the positions with an unsaturated ring would not only solve the bond homolysis problem but it would also provide access to a variety of interesting hydrocarbons in a direct and elegant fashion. We are exploring some of the possibilities.

Experimental Section

All melting points were determined with a Thomas-Hoover oil immersion capillary melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian XL200 spectrometer (chemical shifts in ppm downfield from internal tetramethylsilane at 0.000 ppm); proton decoupled ^{13}C NMR spectra were recorded on a JEOL FX90Q or a Varian XL400. Chemical shifts are referenced to the central resonance of the solvent multiplet ($CDCl_3$ 77.000 ppm; acetone-d_6 29.800 ppm; DMSO-d_6 39.500 ppm). ^2H NMR spectra were obtained on a Varian XL400 spectrometer and are referenced to internal $CDCl_3$ (7.24 ppm). Mass spectra were obtained on AEI MS902 or Finnigan 3300 mass spectrometers. GC analyses were performed with a carbowax-20M capillary column maintained at 150 °C.

Polygram Sil G/UV_{240} plates were used for TLC; Baker silica gel (ca. 40 μm average particle diameter) activated at 120 °C for 12 h was used for flash chromatography. Dimethylformamide (DMF) was dried over CaH_2 for at least 24 h and filtered before use. Benzene and THF were freshly distilled from Na/benzophenone ketyl.

The pyrolysis experiments were performed with use of an unpacked quartz tube (40 cm × 2.0 cm i.d.) heated over the central 30 cm by a Lindberg Sola Basic horizontal tube oven. Pressures were measured with a Hg manometer located between the pump and the trap on the receiver. Temperatures were measured with a Chromel-Alumel thermocouple placed outside the tube and near the center of the hot zone (reference junction at 0 °C).

Compounds to be pyrolyzed were placed in a stainless steel boat and introduced to the tube, which was sealed with a ground-glass stopper and wrapped with heating tape on the surface outside the furnace. The receiving end of the tube was fitted with a vacuum distillation adapter and a small one-necked round-bottomed flask or similar trap. The apparatus was evacuated, and the oven was heated to the desired temperature. After the temperature had stabilized, a liquid N_2 or acetone/CO_2 bath was placed around the receiver, and the inlet side of the apparatus was gradually heated until an increase in pressure was observed. Typically, the pressure rose to a maximum and then decreased; the reported pressures are the maxima observed during an experiment. When the pressure had decreased to a minimum, the inlet was heated strongly for ca. 15 min, and then the entire apparatus was allowed to cool. The pyrolysate was rinsed from the receiving end of the tube with CH_2Cl_2 into a tared flask and analyzed or product isolated as detailed below.

Details of the preparations of and analytical data for 2-methyl-6-nitroacetanilide (**2a**), 2-iodo-3-methylnitrobenzene (**3a**), 6,6′-dimethyl-2,2′-dinitrobiphenyl (**4a**), and 1,10-dimethylbenzo[c]cinnoline (**1a**) are provided in the Supplementary Material.

2-Iodo-3-ethylnitrobenzene (3b). A 250-mL round-bottomed flask equipped with magnetic stirrer and condenser was charged with 2-methyl-6-nitroacetanilide (**2b**)[7b] (20.8 g, 100 mmol) and

(18) A referee of this paper has suggested that although there is evidence for unsymmetrical cleavage of azoalkanes, the mechanism for aromatic azo compounds is still uncertain. In our analysis we have assumed analogous stepwise one-bond cleavages. We rejected the synchronous mechanism because it appeared either to force the already crowded alkyl groups into each other, or if this were to be avoided, to force the extruded nitrogen into an electronically excited state. As the reviewer noted, if the synchronous mechanism were to apply, it is no longer clear that the alkyl–benzyl cleavage should be competitive. The success of the one-bond cleavage analysis might be taken as indirect evidence for unsymmetrical cleavage.

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concentrated HCl (120 mL). The mixture was heated to reflux with swirling to minimize the amount of foaming. All of the solids dissolved. The solution was refluxed for 4 h and then cooled to 8–10 °C with an ice–water bath. A bright orange solid formed. The suspension was treated with a solution of $NaNO_2$ (7.59 g, 110 mmol) in 30 mL of H_2O, the addition proceeding at such a rate that the temperature remained below 10 °C. During the addition all of the solids dissolved and a brown-yellow solution resulted. This was stirred in the ice bath for 30 min and then poured into a solution of KI (33.2 g, 200 mmol) in 300 mL of ice–water. A very dark solution resulted. After 15 min, excess solid $NaHSO_3$ was added. A dark oil separated, which was extracted into 500 mL of Et_2O. The organic layer was washed with 4 N HCl (2 × 500 mL), 10% $NaHSO_3$ (2 × 500 mL), and brine (1 × 500 mL). The mixture was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to afford an orange oil (20.83 g). This product was purified by vacuum distillation. The product boiling at 115–117 °C (0.85 mm) weighed 18.44 g (67%): ^1H NMR ($CDCl_3$) δ 7.37 (s, 3 H), 2.87 (q, 2 H, J = 7.4 Hz), 1.22 (t, 3 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 155.3, 149.8, 130.9, 128.9, 121.6, 91.2, 35.2, 14.3; mass spectrum, m/z (intensity) 278 (8.82), 277 (100.0), 260 (43.72), 230 (12.72), 105 (10.67), 104 (72.65), 103 (66.34), 102 (16.32), 91 (21.81), 89 (11.81), 78 (39.21), 77 (45.54), 76 (12.45), 75 (11.01), 63 (21.34), 51 (24.30), 50 (15.35), 43 (16.32), 39 (20.40); mass spectrum, m/z 276.9578, calcd 276.9602 for $C_8H_8INO_2$.

2,2′-Dinitro-6,6′-diethylbiphenyl (4b). A 250-mL round-bottomed flask was charged with 2-iodo-3-ethylnitrobenzene (13.85 g, 50 mmol), dry DMF (100 mL), and Cu powder (14 g). The mixture was refluxed for 4 h, treated with an additional portion of Cu (14 g), and refluxed an additional 4 h. Ether (100 mL) was added to the cooled solution, and the mixture was filtered into a separatory funnel. The inorganic residue remaining in the reaction vessel was rinsed with two additional 100-mL portions of Et_2O. These were combined with the solution in the separatory funnel. The organic layer was washed with H_2O (5 × 500 mL) and brine (1 × 500 mL) and dried ($MgSO_4$), and the solvent was removed to afford a yellow oil (6.91 g). Recrystallization from ca. 25 mL of EtOH (−20 °C) gave 4.16 g of product: mp 81–82 °C; ^1H NMR ($CDCl_3$) δ 8.50 (dd, 2 H, J = 6.0 Hz, J = 3.3 Hz), 7.79 (d, J = 6.0 Hz), 7.77 (d, 2 H, J = 3.3 Hz), 3.06 (q, 4 H, J = 7.4 Hz), 0.97 (t, 6 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 148.4, 144.0, 133.2, 130.5, 128.8, 122.3, 26.0, 14.0; mass spectrum, m/z (intensity) 301 (20.01), 300 (14.58), 254 (94.06), 239 (55.89), 263 (87.78), 222 (100.00), 221 (50.86), 208 (52.78), 197 (50.32), 194 (41.92), 193 (36.69), 191 (37.50), 180 (35.37), 179 (42.39), 178 (65.34), 165 (84.48), 152 (49.68), 115 (35.44); mass spectrum, m/z 300.1109, calcd 300.1110 for $C_{16}H_{16}N_2O_4$; mass spectrum, m/z 301.1183, calcd 301.1188 for $C_{16}H_{17}N_2O_4$.

1,10-Diethylbenzo[*c*]cinnoline (1b). An oven-dried 250-mL three-necked round-bottomed flask equipped with magnetic stirrer, addition funnel, condenser, and N_2 inlet was charged with $LiAlH_4$ (1.85 g, 49 mmol) and anhydrous Et_2O (40 mL). A solution of 2,2′-dinitro-6,6′-diethylbiphenyl (**4b**) (3.00 g, 10 mmol) in dry benzene (50 mL) was added dropwise over a 40-min period. The mixture refluxed gently as the addition proceeded and became dark brown. The mixture was stirred an additional 30 min. Excess H_2O was added carefully, and the yellow supernate was separated from the inorganic residue by gravity filtration. The residue was rinsed with Et_2O, and the solvents were removed in vacuo. The resulting orange oil (2.62 g) was dissolved in 100 mL of Et_2O, and the solution was filtered through a sintered-glass funnel containing 4 cm × 6 cm diameter silica gel. This gave a dark oil upon evaporation of the solvent. Attempted sublimation (100 °C, 0.1 Torr) gave only a yellow liquid condensate on the cold finger. A portion of this material (412 mg) was purified by flash chromatography (SiO_2, 70:30 hexane–EtOAc) to give 320 mg of yellow oil (87% yield), which crystallized on standing: mp 64–75 °C (mixture of enantiomers?); TLC (70:30 hexane–EtOAc) R_f 0.30; ^1H NMR ($CDCl_3$) δ 8.50 (dd, 2 H, J = 6.0 Hz, J = 3.3 Hz), 7.79 (d, 2 H, J = 6.0 Hz), 7.77 (d, 2 H, J = 3.3 Hz), 3.06 (q, J = 7.4 Hz), 0.97 (t, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 146.1, 140.7, 130.8, 128.1, 127.3, 119.0, 27.1, 16.3; mass spectrum, m/z (intensity) 237 (17.34), 236 (73.67), 193 (43.92), 180 (10.70), 179 (54.43), 178 (100.00), 177 (10.57), 176 (11.65), 165 (33.92), 152 (12.34), 89 (10.63), 63 (10.82), 43 (11.71); mass sectrum, m/z 236.1603, calcd 239.1313 for $C_{16}H_{16}N_2$.

Pyrolysis of 1,10-Dimethylbenzo[*c*]cinnoline (1a). The benzocinnoline (1.000 g, sublimed sample) was pyrolyzed at 734 ± 4 °C. NMR analysis of the crude product (850 mg), which was composed of yellow crystals embedded in an oily black solid, showed the ratio of 1,8-dimethylbiphenylene (**6**)–1,10-dimethylbenzo[*c*]cinnoline (**1a**)–9,10-dihydrophenanthrene (**7**) was 71:14:15. This material was loaded onto a column of silica gel with minimal CCl_4 and eluted with hexane. The solvent was removed from the eluate to give a pale yellow solid (616 mg). GC and NMR analysis of this mixture showed it was composed of 80% **6** and 13% **7**. Other compounds constituted <7% of the mixture (assuming equal detector response factors). Quantitative GC analysis showed the sample contained 525 mg of **6** (61% yield; 71% based on consumed **1a**).

Preparative-Scale Pyrolysis of 1,10-Dimethylbenzo[*c*]cinnoline. Pyrolysis of **1a** (6.24g, 30 mmol) at 730 °C (0.6 Torr) produced 5.76 g of crude, dark solid. This and 150 mL of ethylene glycol were placed in a 250-mL one-necked round-bottomed flask equipped with distillation take off and receiver adapters and a receiving flask cooled with an ice–water bath. The pot was heated, and four 50-mL fractions were collected. The pot was replenished with ethylene glycol as needed. The combined distillates were poured into H_2O (200 mL) and extracted with hexane (3 × 100 mL). The combined hexane extracts were washed with brine (4 × 100 mL), dried ($MgSO_4$), and filtered. Removal of the solvent afforded a pale yellow solid (4.29 g), which was recrystallized from 20 mL of CH_3OH (−20 °C) to give pale yellow flakes (2.88 g, 53%): mp 78–79 °C (lit.[22] 80–81 °C); ^{13}C NMR ($CDCl_3$) δ 150.380, 149.979, 130.548, 128.064, 126.832, 114.762, 18.144.

Pyrolysis of 1,10-Diethylbenzo[*c*]cinnoline (1b). Pyrolysis of **1b** (280 mg, 1.19 mmol) at 735 ± 5 °c (1 Torr) produced 216 mg of a thick, black oil. This was loaded onto a column of silica gel, and the column was eluted with hexane until the fastest moving band was completely off the column. Evaporation of the solvent produced a yellow oil (fraction A, 132 mg). Further elution with hexane–EtOAc (70:30) yielded two additional bands (fraction B, 24 mg, R_f 0.11; fraction C, 27 mg, R_f 0.20).

Fraction A was diluted volumetrically and analyzed by GC. Comparison with quantitative standards indicated that the sample contained phenanthrene (**9**) (23 mg, t_R 9.48 min) and 1,8-diethylbiphenylene (**8**) (28 mg, t_R 11.57 min). The remainder of the material was composed of >18 additional compounds, which were not investigated further. The most intense resonances in the ^1H NMR spectrum of this fraction could be superimosed on the spectra of authentic samples of phenanthrene and 1,8-diethylbiphenylene. The spectrum contained less intense peaks in the aromatic region (δ 7.5–7.2), olefinic (δ 6.1–5.2), benzylic (δ 2.8–2.2), and alkyl (δ 1.6–0.9) regions of the spectrum.

Fraction B gave a ^1H NMR spectrum that was clearly that of a mixture. By comparison of the relative intensities of the multiplets, the spectrum could be decomposed into the spectra of its components: compound **1** (37% of the mixture) ^1H MNR ($CDCl_3$) δ 9.048 (2 H, dd, J = 7.7, J = 1.3 Hz), 8.441 (2 H, dd, J = 7.8, J = 1.3 Hz), 8.317 (2 H, apparent t, J = 7.8 Hz); compound **2** (63% Of the mixture) ^1H NMR ($CDCl_3$) δ 8.569 (2 H, d, J = 8.5 Hz), 7.814 (2 H, dd, J = 8.5, J = 7.0 Hz), 7.674 (2 H, d, J = 7.0 Hz), 3.381 (4 H, s). A mass spectrum of this mixture indicated molecular ions were present at m/z 204 and 206. A high-resolution mass spectrum provided exact molecular weights of 204.0688 and 206.0843, corresponding to the formulas $C_{14}H_8H_2$ (calcd 204.0687) and $C_{14}H_{10}N_2$ (calcd 206.0844). On the basis of the above data the structures 4,5-diazapyrene (**11**) and 9,10-dihydro-4,5-diazapyrene (**10**) were assigned.

Fraction C had a complex ^1H NMR spectrum and was not investigated further.

5,7-Dimethyl-5,7-dihydrodibenzo[*c*,*e*]thiepin 6,6-Dioxide (20). Under N_2, *n*-BuLi (1.35 mL, 1.51 M solution in hexanes, 2.04 mmol) was added dropwise via a syringe to a stirred solution maintained at −78 °C of 5,7-dihydrodibenzo[*c*,*e*]thiepin 6,6-dioxide **18**[13] (244 mg, 1.00 mmol) in 20 mL of dry THF. Addition of the first equivalent led to a yellow solution; the second equivalent produced an orange color. The solution was stirred for 15 min and then treated with CH_2I (127 μL, 290 mg, 2.04 mmol). The

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resulting yellow solution was warmed to 0 °C and stirred at this temperature for 15 min. The solution, now colorless, was warmed to room temperature and partitioned between Et_2O (30 mL) and 1 M HCl (10 mL). The aqueous layer was removed, and the organic layer was washed with H_2O (1 × 10 mL), saturated $NaHCO_3$ solution (1 × 10 mL), and brine (1 × 10 mL). The solution was dried ($MgSO_4$), and the solvent was evaporated to give a white solid (282 mg, 104%). ^1H NMR analysis showed that this consisted of a cis–trans (40:60) mixture of the dimethyl compounds.

The dioxide **20a** was prepared by dissolving the crude solid in a solution of ca. 10 mg of Na in 70 mL of absolute EtOH and refluxing the solution for 4 h. Extractive workup and chromatography led to 152 mg (56%): mp 205–208 °C; ^1H NMR ($CDCl_3$) δ 7.52–7.45 (8 H, m), 4.00 (2 H, q, J = 7.0 Hz), 1.76 (6 H, d, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 140.3, 132.3, 129.0, 128.8, 126.3, 56.4, 8.1; mass spectrum, m/z (intensity) 273 (1.84), 272 (1.03), 222 (1.81), 209 (8.24), 208 (47.93), 207 (8.59), 194 (19.96), 193 (100.00), 192 (7.36), 191 (7.82), 179 (25.45), 178 (57.59), 165 (12.60); mass spectrum, m/z 272.0875, calcd 272.0871 for $C_{16}H_{16}O_2S$.

Dioxide **20b** was prepared by substitution of CH_2OD for EtOH in the above procedure. Recrystallization from 95% EtOH gave white flakes: 48%, mp 212–214 °C; ^1H NMR ($CDCl_3$) δ 7.52–7.45 (8 H, m), 1.76 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 140.3, 132.3, 129.9, 129.0, 128.1, 126.4, 56.1 (t, J = 21 Hz), 8.0; mass spectrum, m/z (intensity) 275 (0.26), 274 (0.55), 211 (6.99), 210 (41.79), 208 (11.0), 196 (15.51), 195 (100.00), 194 (6.44) 193 (10.01), 181 (8.68), 180 (52.53), 179 (11.81), 178 (5.27), 166 (7.77), 97 (5.58), 90 (6.07).

Pyrolysis of 20b at 737 °C. Pyrolysis of 101 mg (0.37 mmol) of **20b** at 737 ± 7 °C (0.12 Torr) produced 73 mg of a colorless oil. GC indicated that the mixture contained six components, although more than 90% of the peak area was due to two components. A, t_R 6.25 min, area 62.6% of total; B, t_R 9.17 min, area = 29.0% of total. GCMS was used to identify A as 9,10-dimethyl-9,10-dihydrophenanthrene-d_2 and B as phenanthrene-d_2. A: mass spectrum, m/z (intensity) 211 (2.4), 210 (20.0), 196 (12.6), 195 (100.0), 181 (12.6), 180 (79.8), 179 (16.3), 166 (10.2), 96 (10.2), 90 (17.5), 83 (17.9), 77 (12.6). B: mass spectrum, m/z (intensity) 181 (13.6), 180 (100.0), 179 (13.6), 178 (15.3), 90 (23.5), 89 (15.3), 77 (24.0). Since mass spectra of polycyclic species are known[16] to give fragment ions in which H atom scrambling has occurred, mass spectrometry could not be used to determine the location of the labels.

The ^1H NMR ($CDCl_3$) spectrum of the mixture clearly established that the labels were located on C9 and C10 of the 9,10-dihydro-9,10-dimethylphenanthrene; the spectrum had a slightly broadened methyl singlet at δ 1.052. The assignment was corroborated by its ^{13}C NMR spectrum ($CDCl_3$), which displayed a triplet at δ 40.156, and by ^2H NMR ($CHCl_3$), which exhibited a singlet at 2.876 ppm.

The location of the label on the phenanthrene-d_2 was established in an analogous manner. No signal for the protons on C9 or C10 was observed in the ^1H NMR of the mixture, but this region of the spectrum was partially obscured by aromatic resonances due to 9,10-dihydro-9,10-dimethylphenanthrene-*9,10-d_2*. However, the ^{13}C and ^2H NMR spectra provided convincing evidence that the label was located exclusively at C9 and C10. The C9–C10 resonance, in addition to being of low intensity due to the loss of NOE upon substitution by deuterium, was shifted upfield from 126.882 ppm (unlabeled phenanthrene) to 126.634 ppm. This isotope-induced chemical shift has been observed previously[24] in phenanthrene-*9,10-d_2*. A similar isotope-induced chemical shift, also previously observed was seen in the resonance due to C9a and C10a, which was shifted upfield from 131.986 (unlabeled) to 131.919. The aromatic region of the ^2H NMR contained only a major resonance at 7.851 pm (relative intensity 92.7). A smaller resonance at 7.693 ppm (relative intensity 7.3) is due to an impurity.

Pyrolysis of 5,7-Dimethyl-5,7-dihydrodibenzo[*c*,*e*]thiepin 6,6-Dioxide at 530 °C. The sulfone (102 mg, 0.37 mmol) was pyrolyzed (530 °C, 0.2 Torr) by using the usual procedure. A colorless oil (81 mg) was collected. Flash chromatography on a silica gel column with CCl_4 elution gave 68 mg of a colorless oil identified as 9,10-dimethyl-9,10-dihydrophenanthrene by analysis of its ^{13}C NMR spectrum and comparison of its ^1H NMR data with published data:[23] ^1H NMR ($CDCl_3$) δ 7.82–7.72 (2 H, m), 7.36–7.18 (6 H, m), 2.85 (2 H, q, J = 6.8 Hz), 1.08 (6 H, d, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 140.53, 132.19, 129.07, 127.76, 162.78, 123.61, 40.82, 21.81.

Supplementary Material Available: Improved procedures for the preparation of **2a**, **3a**, **4a**, and **1a** (3 pages). Ordering information is given on any current masthead page.

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Formation of Fused Tricyclic Azetidinones and Pyrrolidinones by Intramolecular S_H2 Processes[1]

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Treatment of a variety of suitably substituted sulfides of *N*-(*o*-halobenzyl)- or *N*-(*o*-halophenyl)azetidinone (e.g., **4** and **8**) and -pyrrolidinone (e.g., **12** and **14**) systems with either tributylstannane or tributyltin deuteride affords, by aryl radical substitution at the sulfur atom, the corresponding tricyclic azetidinones (**21** and **26**) and pyrrolidinones (**38** and **47**). The reactions with tributyltin deuteride give, in addition to the cyclized product, products arising through competing intramolecular hydrogen atom migration processes. The approximate rate constants, k_c for ring closure and $k_{1,x}$ (x = 5–7) for unimolecular hydrogen atom transfer, have been determined by comparison with either k_H or k_D, the rate constants for reactions of aryl radicals with tributylstannane or tributyltin deuteride, respectively.

Numerous recent examples[2] have illustrated the increasing importance of free-radical cyclization in synthetic chemistry. Most of them involve intramolecular homolytic addition processes as key steps in the synthesis of carbo-

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