4 + 1 Radical Annulations with Isonitriles: A Simple Route to Cyclopenta-Fused Quinolines

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Abstract: Sunlamp irradiation of 1-substituted 5-iodo-1-pentynes, 5 equiv of phenyl isocyanide, and 1.5 equiv of hexamethylditin in *tert*-butylbenzene (0.01–0.025 M) at 150 °C produces 9-substituted 2,3-dihydro-1*H*-cyclopenta[*b*]quinolines in 36–70% yields. A mechanistic proposal for this first example of a 4 + 1 radical annulation includes the following: (1) radical addition to an isonitrile, (2) cyclization of the resulting imidoyl radical to the alkyne, (3) addition of the so-formed vinyl radical to the aromatic ring, and (4) rearomatization. When substituted isonitriles (*p*-F, *p*-OMe, *m*-F) are employed, the major unrearranged products are accompanied by 7–30% of rearranged products. Independent generation of a proposed intermediate suggests that the rearranged products arise by initial closure of the vinyl radical to form a five-membered ring, followed by C–N bond cleavage and recyclization.

Introduction

The sequencing of radical reactions is emerging as a powerful strategy for the rapid construction of diverse classes of molecules.[2] Radical annulations, which sequence an addition reaction before a cyclization, provide direct entries to functionalized five-membered rings from acyclic precursors.[3] As Figure 1 illustrates, all existing radical annulations are of the 3 + 2 (or, more recently, 4 + 2[3i,k]) class.[4] While a number of reagents have been used as equivalents of the synthon **1**, an alkene **3** is invariably used as the two-atom component because it is naturally suited as a vicinal radical acceptor/radical donor (see synthon **2**). The lower half of Figure 1 introduces a strategy for conducting 4 + 1 annulations that combines synthon **4** with a geminal radical acceptor/radical donor **5**. Literature precedent[5-7] indicates that either an isonitrile **6** or carbon monoxide[8,9] (**7**) should serve as the actual reagent equivalent of synthon **5**. We now describe a one-step synthesis of cyclopentaquinolines from isonitriles. This is the first example of a 4 + 1 radical annulation, and it illustrates that it should be possible to develop a whole class of *n* + 1 radical annulations.

Results and Discussion

Preliminary experiments conducted by heating iodopentyne (**8a**), phenyl isocyanide (**9**), and tributyltin hydride in benzene at 80 °C were not encouraging (Figure 2). However, we were able to isolate small amounts of a highly UV-active product that we quickly identified as the known quinoline **10a**.[10] Despite the presence of tin hydride, **10a** is not a reduction product, but instead it maintains the oxidation state of the starting materials. By individually changing the reaction variables (temperature, concentration, stoichiometry, added reagents), we identified conditions that produced useful amounts of **10a**. From these experiments, we learned the following: (1) The concentration of the reaction is very important. Higher yields are obtained at lower concentrations. (2) The reaction is highly temperature sensitive. Temperatures well above 80 °C are required to produce significant yields of **10a**. (3) Excess isonitrile is required, probably because it suffers thermal decomposition during the reaction.

When a mixture of 1 equiv of **8a** (0.025 M), 5 equiv of phenyl isocyanide, 1.5 equiv of tributyltin hydride, and 0.25 equiv of azobisisobutyronitrile (AIBN) was heated at 150 °C in a sealed tube in benzene for 6 h, iodide **8a** was consumed and we isolated **10a** in 30% yield after flash chromatography. An analysis of a crude reaction in C_6D_6 indicated that a large amount (>30%) of 1-pentyne also formed. This volatile product results from reduction of the pentynyl radical by tin hydride. We isolated much better yields of **10a** when we substituted hexamethylditin for tributyltin hydride, provided that we irradiated the heated reaction with a sunlamp. Under a standard set of conditions, sunlamp irradiation of a *tert*-butylbenzene solution (150 °C) of **8a** (0.025 M), **9** (5 equiv), and hexamethylditin (1.5 equiv) for 38 h gave **10a** in 63% isolated yield. Little or no 1-pentyne formed in this reaction, and no other low molecular weight products were evident by ^{1}H NMR analysis or by chromatography. However, there was a significant

(1) Dreyfus Teacher–Scholar, 1986–1991. NIH Research Career Development Awardee, 1987–1992. ICI Awardee, 1990.

(2) (a) Curran, D. P. *Synthesis* **1988**, Part 1, 417; Part 2, 489. (b) Curran, D. P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, Vol. 4, Chapter 4.2.6, in press.

(3) (a) Keck, G. E.; Burnett, D. A. *J. Org. Chem.* **1987**, *52*, 2958. (b) Barton, D. H. R.; daSilva, E.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1988**, 285. (c) Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 980. (d) Curran, D. P.; Chen, M.-H. *J. Am. Chem. Soc.* **1987**, *109*, 6558. (e) Curran, D. P.; Chen, M.-H.; Spletzer, E.; Seong, C. M.; Chang, C.-T. *J. Am. Chem. Soc.* **1989**, *111*, 8872. (f) Curran, D. P.; van Elburg, P. *Tetrahedron Lett.* **1989**, *30*, 2501. (g) Feldman, K. S.; Romanelli, A. L.; Ruckel, R. E., Jr.; Miller, R. F. *J. Am. Chem. Soc.* **1988**, *110*, 3300. (h) Miura, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 5135. (i) Feldman, K. S.; Vong, A. K. K. *Tetrahedron Lett.* **1990**, *31*, 823. (j) Newcomb, M.; Kumar, M. U. *Tetrahedron Lett.* **1990**, *31*, 1675. (k) Srikrishna, A.; Hemamalini, P. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2511.

(4) In this new retrosynthetic notation, closed dots (•) represent radical doner sites and open dots (◦) represent radical acceptor sites. See ref 2b and Curran, D. P. *SynLett* **1991**, 63.

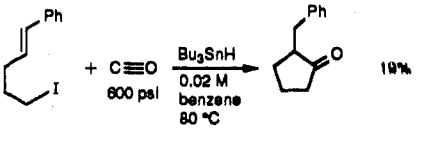
(5) Examples of radical additions to isonitriles: (a) Saegusa, T.; Kobayashi, S.; Ito, Y.; Yasuda, N. *J. Am. Chem. Soc.* **1968**, *90*, 4182. (b) Meier, M.; Rüchardt, C. *Tetrahedron Lett.* **1983**, *24*, 4671. (c) Stork, G.; Sher, M. M. *J. Am. Chem. Soc.* **1983**, *105*, 6765. (d) Barton, D. H. R.; Ozbalik, N.; Vacher, B. *Tetrahedron* **1988**, *44*, 3501.

(6) Structure of imidoyl radicals: (a) Blum, P. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1313. (b) Davies, A. G.; Nedelec, J.-Y.; Sutcliffe, R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 209.

(7) Additions and cyclizations of imidoyl radicals: (a) Leardini, R.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1320. (b) Leardini, R.; Nanni, D.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1591. (c) Leardini, R.; Nanni, D.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Chem. Commun.* **1989**, 757. (d) Leardini, R.; Nanni, D.; Tundo, A.; Zanardi, G. *Gazz. Chem. Ital.* **1989**, *119*, 637. (e) Bachi, M.; Denenmark, D. *J. Am. Chem. Soc.* **1989**, *111*, 1886. (f) Bachi, M.; Denenmark, D. *J. Org. Chem.* **1990**, *55*, 3442.

(8) Leading reference for additions to CO: Ryu, I; Kusano, K.; Ogawa, A.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 1295.

(9) We have conducted a preliminary experiment that shows that annulations with CO should be possible.



(10) Borsche, W. *Ann.* **1910**, *377*, 70.

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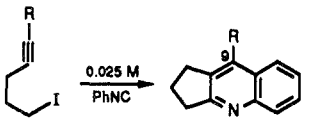
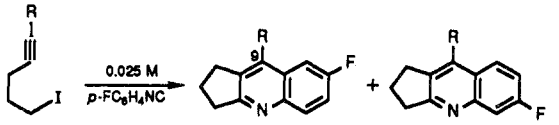
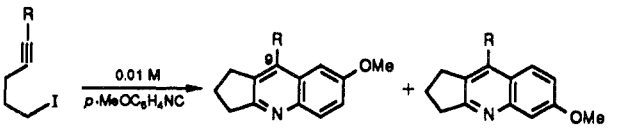
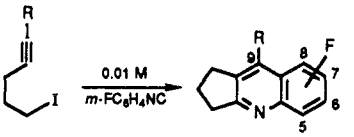
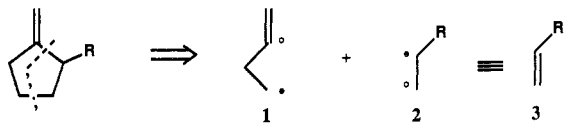
Table I. Cyclopentaquinolines from 4 + 1 Annulations

entry	iodide	isonitrile	products				isolated yield (ratio)
							
1	**8b**, R = CH_3	**9**	**10b**				70
2	**8c**, R = CH_2Ph	**9**	**10c**				36
3	**8d**, R = Ph	**9**	**10d**				55
							
4	**8a**	**11**	**12a**	**13a**			56 (85/15)
5	**8b**	**11**	**12b**	**13b**			49 (80/20)
6	**8d**	**11**	**12d**	**13d**			57 (93/7)
							
7	**8a**	**14**	**15a**	**16a**			59 (86/14)
8	**8b**	**14**	**15b**	**16b**			62 (79/21)
9	**8d**	**14**	**15d**	**16d**			48 (91/9)
							
			8-F	6-F	7-F	5-F	
10	**8a**	**17**	**18a**	**13a**	**12a**	**19a**	64 (46/32/11/11)
11	**8b**	**17**	**18b**	**13b**	**12b**	**19b**	60 (43/27/20/10)

3 + 2 Radical Annulations



4 + 1 Radical Annulations

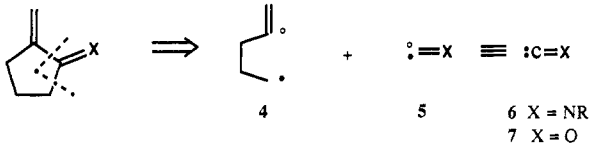


Figure 1.

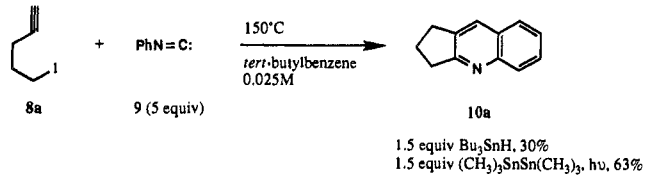


Figure 2.

amount of polar, high molecular weight material that probably resulted from thermal decomposition of the isonitrile.

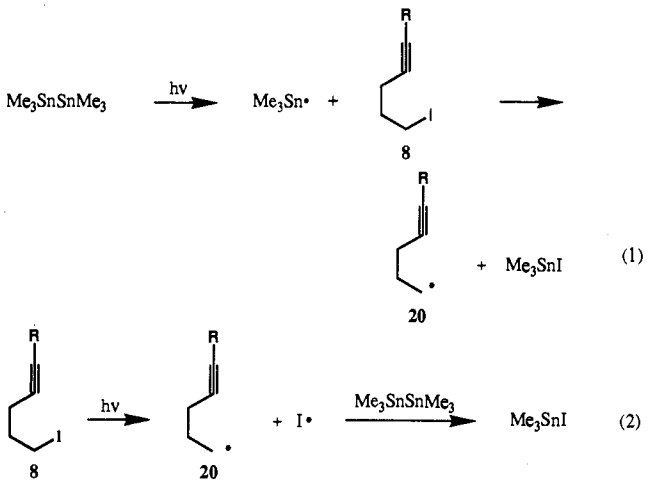
We surveyed the generality of this procedure by reacting several iodopentynes with phenyl isocyanide (**9**), *p*-fluorophenyl isocyanide (**11**), *p*-methoxyphenyl isocyanide (**14**), and *m*-fluorophenyl isocyanide (**17**). Table I summarizes the results of this survey. All of the products in this table were isolated in pure form, and their structures were identified by standard spectroscopic techniques.[11]

For identifying regioisomers (especially in entries 10 and 11), ^{19}F couplings to ^{1}H and ^{13}C were useful, as were nuclear Overhauser effect (NOE) experiments. The Experimental Section contains pertinent results from these experiments. When heated with phenyl isocyanide, terminally substituted iodopentynes **8b–d** produced 9-substituted cyclopenta-fused quinolines **10b–d** (entries 1–3). With *p*-fluorophenyl isocyanide (**11**), two separable regioisomers (**12** and **13**) formed in ratios that varied slightly as a function of the alkyne substituent (entries 4–6). The minor regioisomer **13** is a rearranged product—the orientation of the C–N bond and the fluorine has changed from para to meta. Qualitatively similar results were obtained with *p*-methoxyphenyl isocyanide (**14**); the major product **15** was accompanied by lesser amounts of the rearranged product **16** (entries 7–9). Finally, the use of *m*-fluorophenyl isocyanide (**17**) gave rise to a mixture of four products (entries 10 and 11): two unrearranged (**18** and **13**), and two rearranged (**12** and **19**). Again, the unrearranged products predominated. For each of the three isonitriles, the same trend was observed; the amount of rearranged product decreased in the series **8b** (R = Me) > **8a** (R = H) > **8d** (R = Ph).

This new quinoline synthesis consists of a fascinating sequence of radical reactions that is dissected in eqs 1–13. The 4 + 1 radical annulation is an integral part of this sequence. We envision that radical **20** may be formed either by photolytic cleavage of the ditin, followed by iodine abstraction (eq 1) or by direct photolytic cleavage of the C–I bond (eq 2).[12] In the latter case, the ditin

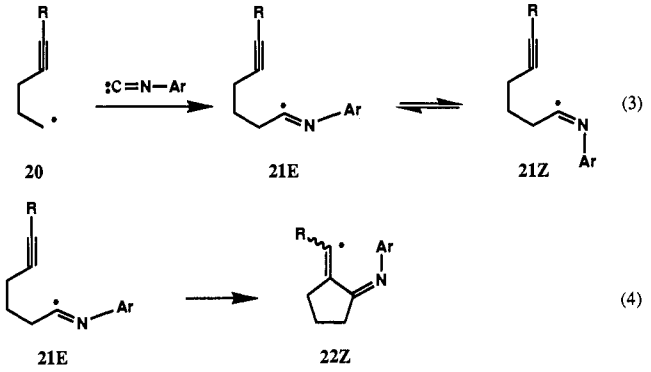
(11) Where possible, spectroscopic and physical properties were compared with literature data **10b**: Treibs, W.; Kempter, G. *Chem. Ber.* **1959**, *92*, 601. **10d**: Fehnel, E. A. *J. Org. Chem.* **1966**, *31*, 2899. **15a** and **16a**: Kazoko, O.; Hiroko, S.; Yujiro, N. *Nippon Kagaku Kaishi* **1989**, 846 (*Chem. Abstr.* **1989**, *111*, 173960b). **12a**: Yen, V. Q.; Buu-Hoi, N. P.; Xuong, N. D. *J. Org. Chem.* **1958**, *23*, 1858.

(12) Curran, D. P.; Chen, M.-H.; Kim, D. *J. Am. Chem. Soc.* **1989**, *111*, 6265.



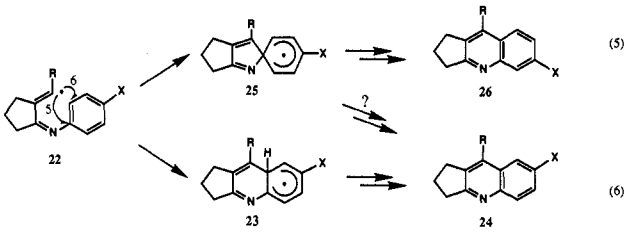
scavenges atomic (or molecular) iodine. Radical generation is followed by three successive, precedented carbon–carbon-forming reactions: addition of an alkyl radical to an isonitrile,[5] cyclization of an imidoyl radical to an alkyne,[7] and cyclization of a vinyl radical to a phenyl ring.[13] Ultimately, an oxidation is required to form the final product.

Addition of **20** to the isonitrile gives radical **21** (eq 3). Like vinyl and acyl radicals, such imidoyl radicals are bent rather than linear[6] and the structure of the product dictates that cyclization must occur predominantly in a 5-exo fashion to form ***22Z*** (eq 4).



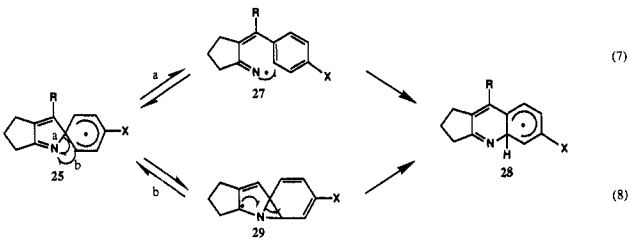
There are no confirmed examples of 5-exo ring openings of vinyl radicals, so we believe that this cyclization is irreversible. We do not know whether ***21E*** is formed kinetically on addition and it cyclizes more rapidly than it interconverts with ***21Z*** or whether ***21E*** and ***21Z*** are in rapid equilibrium and cyclization occurs through ***21E*** (Curtin–Hammett kinetics).[14] Related disubstituted vinyl radicals have very low inversion barriers (<5 kcal/mol),[15] and cyclizations cannot usually compete with isomerizations. Compared to vinyl radicals, imidoyl radicals should have higher inversion barriers[16] (the electronegative nitrogen pyramidalizes the radical). But it is by no means clear that these barriers are sufficiently high so that, if ***21E*** were formed kinetically, it could not isomerize to ***21Z***. To further cloud the isomerization picture, we cannot rule out the possibility that ***21Z*** does cyclize to some extent but that the product radical decomposes by nonproductive pathways because further cyclization to the aromatic ring is geometrically prohibited. To understand the details of this cyclization, we need a better understanding of the factors that control equilibria and rates of reaction of stereoisomeric sp^2-hybridized radicals.

Cyclic vinyl radical **22** is certainly rapidly inverting,[15] and the depicted isomer can cyclize to either of two positions on the aromatic ring (eqs 5 and 6). Closure to the ortho position forms six-membered-ring product **23**, which is then ultimately converted to the unrearranged product **24** (eq 6). Rearranged product **26**



must ultimately arise from cyclization of **22** to the ipso position to form five-membered-ring product **25** (eq 5). That such vinyl radicals can close to either the ipso or the ortho position is a rather general observation,[7,17] and although ipso product **25** may lead to **24** as well as **26**, there is some evidence that it does not.[7b]

We envision at least two ways (eqs 7 and 8) by which radical **25** can isomerize to **28**, the probable precursor of rearranged product **26**. The first possibility is that **25** may suffer ring opening.



Reverse cyclization to reform vinyl radical **22** is unlikely, but ring opening of **25** with C–N cleavage to give **27** is a reasonable possibility (eq 7). Closure of iminyl radical **27** at the ortho position gives the rearranged radical **28**. Newcomb and co-workers have recently shown that aminyl radical cyclizations are surprisingly easily reversed,[18] and this is the closest current precedent for the reverse cyclization of radical **25** to give **27**. The second possibility is that radical **25** undergoes a (reversible?) 3-exo closure to give strained intermediate **29** (eq 8). 3-Exo opening of **29** by cleavage of the intraannular bond then gives **28**. Such ring expansions are well precedented for simple β multiply bonded alkyl radicals,[19] although we know of no examples where allyl or dienyl radicals participate.

A simple experiment proved that if **27** were formed, it would ultimately be converted to **28** under the reaction conditions (eq 9). Cyclization of bromide **30a** under the standard conditions provided a 6/1 mixture of quinoline **10d** and the reduced product. Quinoline **10d** was isolated in 68% yield. It is highly probable that the vinyl radical derived from bromine abstraction of **30** cyclizes to form **27** (R = Ph, X = H). Thus, **27** is a viable, but not obligatory, intermediate in the conversion of **25** to **28** (eq 7).

Cyclization of the *p*-fluoro derivative **30b** provided a regiochemical marker: 6-fluoro isomer **31** was the only product formed, and it was isolated in 76% yield. Thus, if radical **27** is formed in the radical annulation, it leads only to the rearranged product

(13) For related cyclizations of alkyl and vinyl radicals to make quinoline derivatives, see ref 7.

(14) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

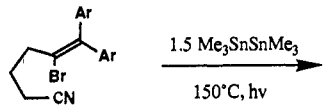
(15) (a) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147. (b) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Chem. Phys.* **1964**, *40*, 213. (c) Stork, G.; Baine, N. H. *Tetrahedron Lett.* **1985**, *26*, 5927. (d) In direct contrast to imodoyl radicals, β-stannyl vinyl radicals cyclize exclusively through the *Z* isomer. Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2829.

(16) INDO calculations on •CH=NH predict that the *E* isomer is more stable than the *Z* isomer by ~2.5 kcal/mol and that the barrier to interconversion is ~10 kcal/mol. See ref 6a.

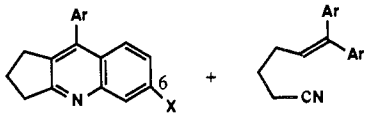
(17) For related ipso closures of aryl radicals, see: (a) Snieckus, V.; Cuevas, J.-C.; Sloan, C. P.; Liu, H.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 896. (b) Grimshaw, J.; Haslett, R. J. *J. Chem. Soc., Perkin Trans. 1* **1980**, 657. (c) Togo, H.; Kikuchi, O. *Heterocycles* **1989**, *28*, 373.

(18) Newcomb, M.; Deeb, T. M.; Marquardt, D. J. *Tetrahedron* **1990**, *46*, 2317.

(19) (a) Dowd, P.; Choi, S.-C. *Tetrahedron* **1989**, *45*, 77. (b) Beckwith, A. L. J.; O'Shea, D. M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565. (c) The closest precedent involves 3-exo closure of an alkyl radical to the nitrogen end of a C=N bond. Choi, G. Ph.D. Thesis, University of Pittsburgh, 1990.



30a Ar = C_6H_5
30b Ar = p-FC_6H_4

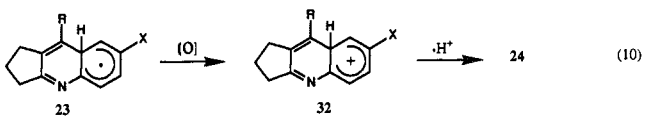


(9)

10d X = H, Ar = C_6H_5
31 X = F, Ar = p-FC_6H_4

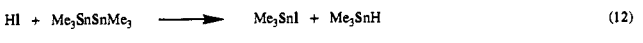
26 and not the unrearranged product **24**.

Accepting that radicals **23** and **28** are the precursors of the unrearranged **24** and rearranged **26** products, then the last step must be an oxidation (eq 10). Even under reductive conditions,

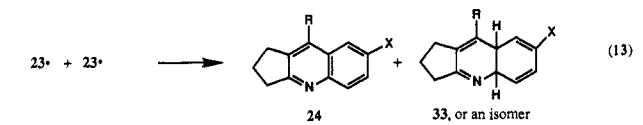


23 32 (10)

(11)



(12)



(13)

the formation of rearomatized products after radical additions to aromatic rings is common;[17,20] however, the oxidant is not immediately obvious. One possibility is that oxygen is present in trace amounts. Although we do not rigorously remove oxygen by freeze/thaw techniques, our reactions are degassed, and we do not believe that sufficient oxygen remains to conduct stoichiometric oxidations. The possibility that the starting iodide is an oxidant can be discarded because this would result in a chain,[21] and stoichiometric quantities of tin reagents would not be required. A second, related possibility is that trimethyltin iodide is the oxidant (eq 11). This would also result in a chain, but the tin reagent would be consumed as a reagent because the HI formed on deprotonation of **30** would react with the hexamethylditin to form trimethyltin iodide and trimethyltin hydride (eq 12). If this chain is occurring, we do not believe that it is very efficient. The high temperature and long time requirements make efficient chains seem unlikely, and we have no evidence that trimethyltin hydride accumulates as a reaction product. A final possibility is that oxidation occurs by radical disproportionation (eq 13). Disproportionation of two molecules of **23** would give **24** and dihydroquinoline **33** or a double bond isomer. Since the yield of quinoline often exceeds 50%, we must then postulate that the dihydroquinolines are air oxidized to **24** during the reaction or workup. While this oxidation is very likely,[22] there is no evidence for dihydroquinoline products when reactions conducted in C_6D_6 are subjected to NMR analysis prior to exposure to air.

In conclusion, the reactions of iodopentynes with aryl isonitriles provide a convenient, one-step synthesis of cyclopenta-fused isoquinolines. The success of these reactions raises a variety of interesting mechanistic and structural questions about the intermediate radicals. Of more immediate importance, it demonstrates that 4 + 1 radical annulations of isonitriles are feasible and variations on this general theme are almost certainly possible. For example, by an appropriate choice of substituents and reactions conditions, it should be possible to intercept the radical **22** directly after the 4 + 1 annulation (steps 3 and 4). This would provide a new route to imine derivative of cyclopentanones.

Experimental Section

General Procedure. To a flat flask (Pyrex, outside dimensions 36 × 160 × 8 mm, wall thickness 1 mm) under N_2 was added a 1-substituted-5-iodo-1-pentyne (0.25 mmol), an isonitrile (1.25 mmol), hexamethylditin (0.375 mmol), and *tert*-butylbenzene (10 mL). The mixture was irradiated with a 275-W sunlamp (GE RSK6) at 150 °C (silicone oil bath, about two-thirds of the liquid body higher than the oil level) for 12 to 60 h until the iodopentyne was consumed (followed by ^1H NMR). The reaction was then cooled to room temperture, diluted with ether (15 mL), shaken with 2 N HCl (10 mL), filtered through a sintered funnel, and separated. The organic layer was extracted with 2 N HCl (10 mL × 4). The combined aqueous phase was neutralized with 6 N NaOH and was extracted with ether (30 mL × 3). The combined ether extract was washed successively with aqueous $NaHCO_3$, H_2O, and brine (30 mL each) and dried over $MgSO_4$. After solvent removal, the residue was purified by chromatography (aluminum oxide 90, EM product) to provide the 9-substituted-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline isomers. If needed, further separation was accomplished by MPLC or HPLC.

2,3-Dihydro-1*H*-cyclopenta[*b*]quinoline (10a): ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (1 H, d, J = 8.5 Hz), 7.90 (1 H, br s), 7.74 (1 H, dd, J = 8.1, 1.3 Hz), 7.62 (1 H, td, J = 7.7, 1.3 Hz), 7.45 (1 H, td, J = 7.5, 1.0 Hz), 3.17 (2 H, t, J = 7.7 Hz), 3.10 (2 H, td, J = 7.5, 1.3 Hz), 2.22 (2 H, qt, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.54, 147.19, 135.26, 129.98, 128.24, 128.04, 127.20, 127.11, 125.20, 34.32, 30.18, 23.29; IR (neat) 3062, 2963, 1502, 1408, 756 cm^{-1}; MS m/e 169 (M), 168 (M − 1, base peak); HRMS for $C_{12}H_{11}N$ calcd 169.0891, found 169.0891.

9-Methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (10b): ^1H NMR (300 MHz, $CDCl_3$) δ 8.01 (1 H, dd, J = 8.3, 1.0 Hz), 7.94 (1 H, dd, J = 8.3, 1.2 Hz), 7.61 (1 H, td, J = 7.6, 1.2 Hz), 7.48 (1 H, td, J = 7.7, 1.0 Hz), 3.17 (2 H, t, J = 7.7 Hz), 3.06 (2 H, t, J = 7.4 Hz), 2.59 (3 H, s), 2.20 (2 H, qt, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.02, 147.49, 138.07, 134.03, 129.21, 128.00, 127.07, 125.23, 123.37, 35.16, 29.66, 23.00, 14.91; IR (neat) 3063, 2955, 1613, 1570, 1507, 1389, 1340, 1215, 1024, 758 cm^{-1}; MS m/e 184 (M + 1), 183 (M, base peak), 182 (M − 1), 168; HRMS for $C_{13}H_{13}N$ calcd 183.1048, found 183.1048.

9-Benzyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (10c): ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (1 H, dd, J = 7.7, 1.0 Hz), 7.92 (1 H, dd, J = 7.7, 1.2 Hz), 7.60 (1 H, td, J = 7.7, 1.2 Hz), 7.42 (1 H, td, J = 7.7, 1.0 Hz), 7.24–7.15 (3 H, m), 7.10 (2 H, d, J = 7.6 Hz), 4.41 (2 H, S), 3.21 (2 H, t, J = 7.7 Hz), 3.05 (2 H, t, J = 7.4 Hz), 2.21 (2 H, qt, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.44, 148.13, 139.94, 138.72, 135.00, 129.37, 128.66 (2 C), 128.24 (2 C), 128.12, 126.66, 126.36, 125.62, 123.95, 35.16, 34.87, 29.77, 23.07; IR (neat) 3072, 2957, 1611, 1577, 1498, 754, 705 cm^{-1}; MS m/e 260 (M + 1), 259 (M, base peak), 258 (M − 1), 181, 168, 91.77; HRMS for $C_{19}H_{17}N$ calcd 259.1361, found 259.1361.

9-Phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (10d): ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (1 H, dd, J = 8.8, 0.8 Hz), 7.64–7.59 (2 H, m), 7.56–7.43 (3 H, m), 7.40–7.35 (3 H, m), 3.24 (2 H, t, J = 7.6 Hz), 2.91 (2 H, t, J = 7.4 Hz), 2.17 (2 H, qt, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_2$) δ 167.40, 147.94, 142.63, 136.72, 133.61, 129.26 (2 C), 128.80, 128.47 (2 C), 128.19, 127.95, 126.17, 125.62, 125.46, 35.20, 30.31, 23.50; IR (neat) 3064, 2973, 1577, 1487, 767, 759, 696 cm^{-1}; MS m/e 246 (M + 1), 245 (M, base peak), 244 (M − 1), 168; HRMS for $C_{18}H_{15}N$ calcd 245.1024, found 245.1024.

7-Fluoro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (12a): ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (1 H, dd, J = 9.1, 5.4 Hz), 7.79 (1 H, s), 7.39–7.29 (2 H, m), 3.12 (2 H, t, J = 7.7 Hz), 3.06 (2 H, td, J = 7.4, 0.8 Hz), 2.19 (2 H, qt, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.44, 159.77 (J_{CF} = 245.3 Hz), 144.54, 136.61, 130.76 (J_{CF} = 9.4 Hz), 129.65 (J_{CF} = 4.4 Hz), 127.98 (J_{CF} = 9.8 Hz), 118.17 (J_{CF} = 24.9 Hz), 110.59 (J_{CF} = 21.9 Hz), 34.48, 30.54, 23.65; IR (neat) 3071, 2955, 1505, 1211, 911, 835 cm^{-1}; MS m/e 188 (M + 1), 187 (M), 186 (M − 1, base peak); HRMS for $C_{12}H_{10}FN$ calcd 187.0797, found 187.0797.

6-Fluoro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (13a): ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (1 H, s), 7.71 (1 H, dd, J = 8.9, 6.1 Hz), 7.64 (1 H, dd, J = 10.4, 2.6 Hz), 7.25 (1 H, td, J = 8.6, 2.6 Hz), 3.15 (2 H, t, J = 7.7 Hz), 3.08 (2 H, t, J = 7.4 Hz), 2.22 (2 H, qt, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.22, 162.53 (J_{CF} = 248.9 Hz), 148.44 (J_{CF} = 8.1 Hz), 135.14, 130.32, 129.21 (J_{CF} = 9.7 Hz), 124.38, 115.75

(20) Takano, S.; Suzuki, M.; Kijima, A.; Ogasawara, K. *Tetrahedron Lett.* **1990**, *31*, 2315.

(21) For an example of how chains can be propagated by electron transfer to iodides, see: Kolt, R. J.; Wayner, D. D. M.; Griller, D. *J. Org. Chem.* **1989**, *54*, 4259.

(22) Francis, R. F.; Crews, C. D.; Scott, B. S. *J. Org. Chem.* **1978**, *43*, 3227.

(J_{CF} = 24.4 Hz), 112.48 (J_{CF} = 19.6 Hz), 34.72, 30.45, 23.68; IR (neat) 3038, 2963, 1632, 1505, 1414, 1223, 911 cm^{-1}; MS *m/e* 188 (M + 1), 187 (M), 186 (M − 1, base peak); HRMS for $C_{12}H_{10}FN$ calcd 187.0797, found 187.0770.

8-Fluoro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (18a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (1 H, s), 7.81 (1 H, d, *J* = 8.5 Hz), 7.53 (1 H, td, *J* = 8.1, 6.1 Hz), 7.13 (1 H, dd, *J* = 9.6, 8.1 Hz), 3.17 (2 H, t, *J* = 7.7 Hz), 3.12 (2 H, td, *J* = 7.5, 1.2 Hz), 2.23 (2 H, qt, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.06, 158.153 (J_{CF} = 253.0 Hz), 148.44, 136.10, 127.86 (J_{CF} = 9.0 Hz), 124.40, 123.50, 118.01 (J_{CF} = 16.2 Hz), 109.44 (J_{CF} = 19.7 Hz), 34.74, 30.73, 23.62; IR (neat) 3033, 2971, 1507, 1188, 810, 758 cm^{-1}; MS *m/e* 188 (M + 1), 187 (M), 186 (M − 1, base peak); HRMS for C_{12} for $C_{12}H_{10}FN$ calcd 187.0797, found 187.0797.

5-Fluoro-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (19a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (1 H, s), 7.52 (1 H, d, *J* = 8.1 Hz), 7.38 (1 H, td, *J* = 7.9, 5.0 Hz), 7.32 (1 H, ddd, *J* = 10.8, 7.7, 1.3 Hz), 3.22 (2 H, t, *J* = 7.7 Hz), 3.11 (2 H, td, *J* = 7.5, 1.2 Hz), 2.23 (2 H, qt, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.58, 157.92 (J_{CF} = 254.4 Hz), 137.54 (J_{CF} = 12.4 Hz), 137.04, 130.23, 129.26, 125.30 (J_{CF} = 7.8 Hz), 123.12 (J_{CF} = 4.8 Hz), 112.70 (J_{CF} = 19.4 Hz), 34.82, 30.63, 23.67; IR (neat) 3031, 2953, 1496, 1250, 1125, 1026, 893, 762 cm^{-1}; MS *m/e* 188 (M + 1), 187 (M, base peak), 186 (M − 1); HRMS for $C_{12}H_{10}FN$ calcd 187.0797, found 187.0779.

7-Fluoro-9-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (12b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (1 H, dd, *J* = 9.1, 5.7 Hz), 7.53 (1 H, dd, *J* = 10.3, 2.7 Hz), 7.37 (1 H, td, *J* = 8.6, 2.7 Hz), 3.15 (2 H, t, *J* = 7.7 Hz), 3.06 (2 H, t, *J* = 7.4 Hz), 2.54 (3 H, s), 2.21 (2 H, qt, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.56, 160.10 (J_{CF} = 244.5 Hz), 144.55, 137.53 (J_{CF} = 4.9 Hz), 134.91, 131.37 (J_{CF} = 9.3 Hz), 127.93 (J_{CF} = 9.1 Hz), 117.74 (J_{CF} = 25.3 Hz), 107.23 (J_{CF} = 22.6 Hz), 35.03, 29.77, 23.06, 15.10; IR (neat) 3036, 2969, 1509, 1215, 1176 cm^{-1}; MS *m/e* 202 (M + 1), 201 (M, base peak), 200 (M − 1), 186; HRMS for $C_{13}H_{12}FN$ calcd 201.0954, found 201.0954.

6-Fluoro-9-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (13b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (1 H, dd, *J* = 9.2, 6.1 Hz), 7.63 (1 H, dd, *J* = 10.3, 2.6 Hz), 7.26 (1 H, td, *J* = 8.7, 2.6 Hz), 3.16 (2 H, t, *J* = 7.7 Hz), 3.05 (2 H, t, *J* = 7.5 Hz), 2.58 (3 H, s), 2.21 (2 H, qt, *J* = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.44, 162.36 (J_{CF} = 249.5 Hz), 148.57 (J_{CF} = 12.2 Hz), 138.43, 133.61, 125.36 (J_{CF} = 9.8 Hz), 124.13, 115.23 (J_{CF} = 24.4 Hz), 112.84 (J_{CF} = 19.9 Hz), 35.23, 29.59, 23.03, 15.14; IR (neat) 3046, 2963, 2925, 1623, 1513, 1216, 1136, 817, 767; MS *m/e* 202 (M + 1), 201 (M), 200 (M − 1), 186 (base peak); HRMS for $C_{13}H_{12}FN$ calcd 201.0954, found 201.0954.

8-Fluoro-9-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (18b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (1 H, d, *J* = 8.4 Hz), 7.49 (1 H, td, *J* = 8.0, 5.7 Hz), 7.10 (1 H, dd, *J* = 12.7, 7.8 Hz), 3.16 (2 H, t, *J* = 7.7 Hz), 3.06 (2 H, t, *J* = 7.4 Hz), 2.73 (3 H, d, *J* = 6.2 Hz) 2.19 (2 H, qt, *J* = 7.6 Hz); ^{13}C NMR (125 MHz; $CDCl_3$) δ 167.82, 159.97 (J_{CF} = 254.8 Hz), 149.78, 137.44, 135.47, 127.52 (J_{CF} = 10.1 Hz), 125.29, 117.91 (J_{CF} = 12.2 Hz), 110.62 (J_{CF} = 22.9 Hz), 35.18, 29.81, 22.72, 18.71 (J_{CF} = 11.9 Hz); IR (neat) 3049, 2961, 1572, 1839, 1221, 1167, 1024, 814, 756 cm^{-1}; MS *m/e* 202 (M + 1), 201 (M), 200 (M − 1), 186 (base peak); HRMS for $C_{13}H_{12}FN$ calcd 201.0954, found 201.0955.

5-Fluoro-9-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (19b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (1 H, d, *J* = 8.3 Hz), 7.40 (1 H, td, *J* = 8.0, 5.3 Hz), 7.31 (1 H, ddd, *J* = 10.7, 7.8, 1.0 Hz), 3.22 (2 H, t, *J* = 7.8 Hz), 3.08 (2 H, t, *J* = 7.4 Hz), 2.59 (3 H, s), 2.21 (2 H, qt, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.53, 158.31 (J_{CF} = 253.8 Hz), 138.24, 137.70 (J_{CF} = 11.4 Hz), 135.31, 129.06 (J_{CF} = 3.4 Hz), 124.79 (J_{CF} = 8.1 Hz), 119.14 (J_{CF} = 3.6 Hz), 112.33 (J_{CF} = 19.6 Hz), 35.37, 29.80, 23.03, 15.35; IR (neat) 3044, 2974, 1517, 1194, 814, 760 cm^{-1}; MS *m/e* 202 (M + 1), 201 (M), 200 (M − 1), 186 (base peak); HRMS for $C_{13}H_{12}FN$ calcd 201.0954, found 201.0959.

7-Fluoro-9-phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (12d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (1 H, dd, *J* = 9.2, 5.6 Hz), 7.54–7.42 (3 H, m), 7.39–7.30 (3 H, m), 7.23 (1 H, dd, *J* = 9.4, 2.8 Hz), 3.20 (2 H, t, *J* = 7.6 Hz), 2.89 (2 H, t, *J* = 7.4 Hz), 2.14 (2 H, qt, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.88, 160.15 (J_{CF} = 246.3 Hz), 144.99, 142.11 (J_{CF} = 4.5 Hz), 136.26, 134.48, 130.97 (J_{CF} = 8.3 Hz), 129.11 (2 C), 128.69 (2 C), 128.21, 127.01 (J_{CF} = 9.7 Hz), 117.98 (J_{CF} = 24.6 Hz), 109.17 (J_{CF} = 22.3 Hz), 35.01, 30.36, 23.49; IR (neat) 3069, 2967, 1629, 1511, 1497, 1217, 833, 708 cm^{-1}; MS *m/e* 264 (M + 1), 263 (M, base peak), 262 (M − 1), 235, 286; HRMS for $C_{18}H_{14}FN$ calcd 263.1110, found 263.1096.

6-Fluoro-9-phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (13d): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (1 H, dd, *J* = 8.3, 2.4 Hz), 7.62 (1 H, dd, *J* = 9.2, 6.1 Hz), 7.55–7.47 (3 H, m), 7.35 (2 H, d, *J* = 7.6 Hz), 7.17 (1 H, td, *J* = 8.6, 2.4 Hz), 3.26 (2 H, t, *J* = 7.6 Hz), 2.90 (2 H, t, *J* = 7.4 Hz), 2.18 (2 H, qt, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.89, 162.49 (J_{CF} = 247.8 Hz), 149.09 (J_{CF} = 10.9 Hz), 142.90, 136.54, 133.19 (J_{CF} = 3.2 Hz), 129.26, (2 C), 128.66 (2 C), 128.24, 127.75 (J_{CF} = 10.1 Hz), 123.31, 115.51 (J_{CF} = 24.6 Hz), 112.61 (J_{CF} = 20.0 Hz), 35.35, 30.26, 23.58; IR (neat) 3047, 2919, 1574, 1208, 862, 818, 756 cm^{-1}; MS *m/e* 264 (M + 1), 263 (M, base peak), 262 (M − 1), 235, 186; HRMS for $C_{18}H_{14}FN$ calcd 263.1110, found 263.1090.

7-Methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (15a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (1 H, d, *J* = 9.1 Hz), 7.76 (1 H, s), 7.26 (1 H, dd, *J* = 9.1, 2.8 Hz), 7.00 (1 H, d, *J* = 2.8 Hz), 3.89 (3 H, S), 3.11 (2 H, t, *J* = 7.6 Hz), 3.04 (2 H, t, *J* = 7.4 Hz), 2.18 (qt, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.34, 157.06, 143.44, 135.87, 129.85, 129.27, 128.24, 120.42, 105.56, 55.42, 34.32, 30.54, 23.65; IR (neat) 3073, 2967, 1507, 1226, 1034, 908, 830 cm^{-1}; MS *m/e* 200 (M + 1), 199 (M, base peak), 198 (M − 1), 184, 156, 128; HRMS for $C_{13}H_{13}NO$ calcd 199.0997, found 199.0997.

6-Methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (16a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (1 H, s), 7.61 (1 H, d, *J* = 8.9 Hz), 7.37 (1 H, d, *J* = 2.4 Hz), 7.11 (1 H, dd, *J* = 8.9, 2.4 Hz), 3.93 (3 H, s), 3.13 (2 H, t, *J* = 7.6 Hz), 3.06 (2 H, t, *J* = 7.4 Hz), 2.20 (2 H, qt, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.83, 160.17, 148.71, 133.50, 130.72, 128.43, 122.51, 118.51, 106.81, 55.51, 34.59, 30.42, 23.71; IR (neat) 2953, 1621, 1415, 1231, 1156, 1029 cm^{-1}; MS *m/e* 200 (M + 1), 199 (M, base peak), 198 (M − 1), 184, 168; HRMS for $C_{13}H_{13}NO$ calcd 199.0997, found 199.0983.

7-Methoxy-9-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (15b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (1 H, d, *J* = 9.1 Hz), 7.26 (1 H, dd, *J* = 9.1, 2.7 Hz), 7.15 (1 H, d, *J* = 2.7 Hz), 3.92 (3 H, s), 3.12 (2 H, t, *J* = 7.7 Hz), 3.02 (2 H, t, *J* = 7.4 Hz), 2.51 (3 H, s), 2.17 (2 H, qt, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.53, 157.03, 143.34, 136.81, 134.32, 130.60, 127.88, 119.60, 102.36, 55.52, 34.91, 29.83, 23.10, 15.11; IR (neat) 2982, 1508, 1226, 1022, 832 cm^{-1}; MS *m/e* 214 (M + 1), 213 (M, base peak), 212 (M − 1), 198, 170; HRMS for $C_{14}H_{15}NO$ calcd 213.1154, found 213.1154.

6-Methoxy-9-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (16b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (1 H, d, *J* = 9.1 Hz), 7.37 (1 H, d, *J* = 2.6 Hz), 7.13 (1 H, dd, *J* = 9.1, 2.6 Hz), 3.93 (3 H, s), 3.13 (2 H, t, *J* = 7.8 Hz), 3.02 (2 H, t, *J* = 7.4 Hz), 2.55 (3 H, s), 2.19 (2 H, qt, *J* = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.12, 159.71, 148.94, 138.59, 132.09, 124.51, 122.02, 117.79, 107.45, 55.44, 35.13, 29.05, 23.03, 15.01; IR (neat) 2951, 1605, 1507, 1419, 1221, 1153, 1019 cm^{-1}; MS *m/e* 214 (M + 1), 213 (M, base peak), 212 (M − 1), 198; HRMS for $C_{14}H_{15}NO$ calcd 213.1154, found 213.1144.

7-Methoxy-9-phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (15d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (1 H, d, *J* = 9.2 Hz), 7.55–7.43 (3 H, m), 7.38–7.36 (2 H, m), 7.28 (1 H, dd, *J* = 9.2, 2.8 Hz), 6.92 (1 H, d, *J* = 2.8 Hz), 3.72 (3 H, s), 3.19 (2 H, t, *J* = 7.6 Hz), 2.87 (2 H, t, *J* = 7.4 Hz), 2.14 (2 H, qt, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.95, 157.19, 143.90, 141.73, 137.03, 134.03, 130.17, 129.20 (2 C), 128.66 (2 C), 128.01, 127.10, 119.96, 104.46, 55.41, 34.94, 30.48, 23.62; IR (neat) 2971, 1620, 1497, 1225, 1022 cm^{-1}; MS *m/e* 276 (M + 1), 275 (M, base peak), 274 (M − 1), 260, 244, 198; HRMS for $C_{19}H_{17}NO$ calcd 275.1310, found 275.1310.

6-Methoxy-9-phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (16d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.42 (5 H, m), 7.37–7.34 (2 H, m), 7.03 (1 H, dd, *J* = 9.2, 2.6 Hz), 3.94 (3 H, s), 3.20 (2 H, t, *J* = 7.6 Hz), 2.88 (2 H, t, *J* = 7.4 Hz), 2.15 (2 H, qt, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.73, 159.88, 149.76, 142.88, 136.99, 131.55, 129.32 (2 C), 128.54 (2 C), 128.00, 126.78, 121.20, 118.07, 107.39, 55.50, 35.34, 30.23, 23.60; IR (neat) 2965, 1622, 1414, 1225, 1032, 733 cm^{-1}; MS *m/e* 276 (M + 1), 275 (M, base peak), 274 (M − 1), 260, 198; HRMS for $C_{19}H_{17}NO$ calcd 275.1310, found 275.1310.

6-Fluoro-9-(4′-fluorophenyl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (31): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (1 H, dd, *J* = 10.2, 2.6 Hz), 7.56 (1 H, dd, *J* = 9.2, 6.1 Hz), 7.34–7.28 (2 H, m), 7.21 (2 H, t, *J* = 8.8 Hz), 7.14 (1 H, td, *J* = 8.9, 2.6 Hz), 3.20 (2 H, t, *J* = 7.7 Hz), 2.86 (2 H, t, *J* = 7.4 Hz), 2.16 (2 H, qt, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.84, 162.59 (J_{CF} = 249.3 Hz), 162.46 (J_{CF} = 249.2 Hz), 149.02 (J_{CF} = 12.2 Hz), 141.82, 133.33, 132.34 (J_{CF} = 5.1 Hz), 130.99 (2 C, J_{CF} = 9.8 Hz), 127.39 (J_{CF} = 9.7 Hz), 123.24, 115.77 (2 C, J_{CF} = 22.0 Hz), 115.62 (J_{CF} = 24.4 Hz), 112.66 (J_{CF} = 21.8 Hz), 35.26, 30.22, 23.52; IR (neat) 3051, 2963, 1607, 1499, 1211, 839 cm^{-1}; MS *m/e* 282 (M + 1), 281 (M, base peak), 280 (M − 1), 186; HRMS for $C_{18}H_{13}F_2N$ calcd 281.1016, found 281.1027.

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Registry No. 8a, 2468-55-5; **8b**, 28077-74-9; **8c**, 132017-60-8; **8d**, 34886-50-5; **9**, 931-54-4; **10a**, 5661-06-3; **10b**, 6829-07-8; **10c**, 132017-61-9; **10d**, 10265-82-4; **11**, 24075-34-1; **12a**, 1717-19-7; **12b**, 132017-

62-0; **12d**, 132017-63-1; **13a**, 132017-64-2; **13b**, 132017-65-3; **13d**, 132017-66-4; **14**, 10349-38-9; **15a**, 61831-48-9; **15b**, 132017-67-5; **15d**, 132017-68-6; **16a**, 30160-18-0; **16b**, 132017-69-7; **16d**, 132017-70-0; **17**, 24075-35-2; **18a**, 132017-71-1; **18b**, 132017-72-2; **19a**, 132017-73-3; **19b**, 132017-74-4; **30a**, 132017-75-5; **30a** (debromo derivative), 14636-27-2; **30b**, 132017-76-6; **30b** (debromo derivative), 132017-78-8; **31**, 132017-77-7; $PhCH{=}CH(CH_2)_3I$, 132017-79-9; 2-benzylcyclopentanone, 2867-63-2.

Absorbance, Light Intensity, Mass Transfer, and Sampling Time Effects in a Proposed Mechanism for the Photolysis of Phenyl Azide

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Abstract: In the concentrated phenyl azide solutions in which Costantino et al. have reported apparent quantum yields for azide disappearance (ϕ_{-PhN_3}) on the order of 1000 and interpreted their results in terms of a branching-chain mechanism, the optical penetration depth is sufficiently small that the proposed chain-initiation reaction is effectively confined to a very thin layer near the front optical window. Simple calculations show that this layer is sufficiently thin that diffusive mass transfer is important on the time scale of the experiments. On the basis of the mechanism of Costantino et al., we develop and investigate a model consisting of three nonlinear integro-partial differential equations accounting for the nonuniform light absorption, photochemical kinetics, and diffusive mass transfer. The dependence of ϕ_{-PhN_3} on initial azide concentration is shown to be in good qualitative agreement with experiment. The model predicts that the apparent quantum yield is sometimes a strong function of the time at which the reaction mixture is sampled. The relatively simple mechanism proposed by Costantino et al. is consistent with their results, as well as the more recent measurements of Liang and Schuster, in which quantum yields in excess of unity were not observed. In terms of the proposed branching-chain mechanism, the apparent discrepancies between the results of Costantino et al. and Liang and Schuster can be attributed to the use of different light intensities.

In large part due to their use as photolabeling agents, polymerization initiators, and cross-linking agents,[1] there has been considerable recent interest in the photochemistry of aryl azides,[2-9] with special emphasis on the photolysis of phenyl azide. Recently, additional interest has developed in this area due to the fact that the photolysis can lead to the formation of poly(1,2-azepines). When the process is performed through a photomask, the oxidation products of the poly(1,2-azepines) can form a patterned, semiconducting polymeric film[10] of interest in microelectronics manufacture.

In dilute solution, the photodecomposition of phenyl azide at 254 nm proceeds with a quantum yield (for the disappearance of phenyl azide) of about 0.5, in both nonpolar ($\phi_{N_2} = 0.53 \pm 0.10$ in hexane at 25 °C and 0.52 ± 0.10 in a matrix of methylcyclohexane at 77 K)[11] and polar ($\phi_{-PhN_3} = 0.57 \pm 0.19$ in deoxygenated acetonitrile)[2] solvents.

Recently, Costantino et al.[2] have reported that, in the photolysis of concentrated ($>10^{-3}$ M) solutions of phenyl azide in acetonitrile, ϕ_{-PhN_3} may exceed 10^4. They have proposed a branching-chain mechanism involving triplet nitrene radicals, a chain-initiation step (1), a chain-branching step (2), and two chain-termination steps (3 and 4), which is proposed to be valid over the entire range of azide concentration. Jenkins et al.[3] have conducted a mechanistic study of the photodecomposition of several substituted phenyl azides in the presence of various triplet sensitizers as well as a known singlet quencher and have concluded that the intermediate nitrene in (1-4) is a triplet species.

$$PhN_3 \xrightarrow{h\nu} PhN + N_2 \quad (1)$$

$$PhN + PhN_3 \rightarrow [X] \rightarrow 2PhN + N_2 \quad (2)$$

$$PhN + PhN_3 \rightarrow Ph{-}N{=}N{-}Ph + N_2 \quad (3)$$

$$2PhN \rightarrow Ph{-}N{=}N{-}Ph \quad (4)$$

Recently, Liang and Schuster[9] and Li et al.[12] have questioned the validity of the mechanism (1-4) at high azide concentrations. Using time-resolved infrared and ultraviolet absorption spectroscopy to monitor the concentration of 1,2-didehydroazepine following flash photolysis of phenyl azide, Li et al. have proposed an alternative mechanism, in which the singlet excited azide undergoes intersystem crossing to an excited triplet azide or loses N_2 to form a singlet nitrene. The latter species may undergo either a reversible isomerization to 1,2-didehydroazepine or intersystem crossing to a triplet nitrene, a species which may also result from loss of N_2 by triplet azide. Li et al. propose that azobenzene is formed by dimerization of two triplet nitrenes and that 1,2-didehydroazepine either reacts with azide to give a (presumably polymeric) tarry substance or is converted to triplet nitrene by a process not involving isomerization to singlet nitrene. At low

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(1) Breslow, D. S. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: New York, 1984.
(2) Costantino, J. P.; Richter, H. W.; Lee Go, C. H.; Waddell, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 1744-1747.
(3) Jenkins, R. F.; Waddell, W. H.; Richter, H. W. *J. Am. Chem. Soc.* **1987**, *109*, 1583-1584.
(4) Waddell, W. H.; Lee Go, C. *J. Am. Chem. Soc.* **1982**, *104*, 5804-5805.
(5) Lee Go, C. H.; Waddell, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 715-718.
(6) Lee Go, C.; Waddell, W. H. *J. Org. Chem.* **1983**, *48*, 2897-2900.
(7) Feilchenfeld, N. B.; Waddell, W. H. *Chem. Phys. Lett.* **1983**, *98*, 190-194.
(8) Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783-3790.
(9) Liang, T.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1987**, *109*, 7803-7810.
(10) Meijer, E. W.; Nijhuis, S.; van Vroonhoven, F. C. B. M. *J. Am. Chem. Soc.* **1988**, *110*, 7209-7210.
(11) Reiser, A.; Marley, R. *Trans. Faraday Soc.* **1968**, *64*, 1806-1815.
(12) Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092-8098.

0002-7863/91/1513-2132$02.50/0