

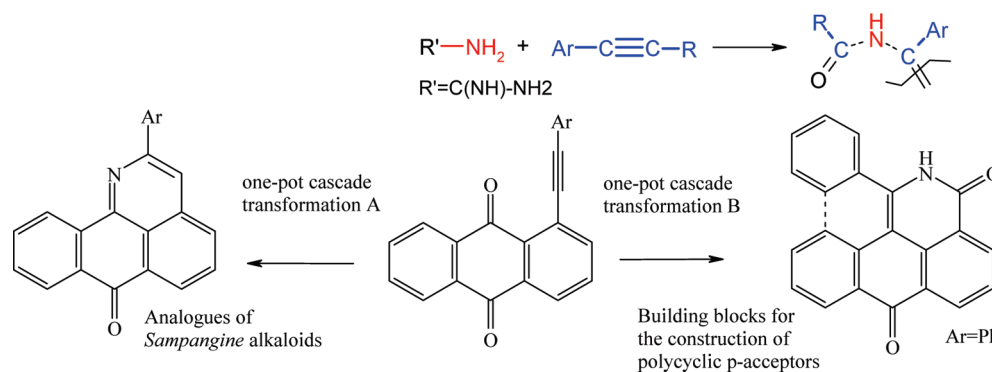
An Unexpected Rearrangement That Disassembles Alkyne Moiety Through Formal Nitrogen Atom Insertion between Two Acetylenic Carbons and Related Cascade Transformations: New Approach to *Sampangine* Derivatives and Polycyclic Aromatic Amides

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This work analyzes multiple new reaction pathways which originate from intramolecular reactions of activated alkynes with the appropriately positioned multifunctional hemiaminal moiety. Combination of experimental substituent effects with Natural Bond Orbital (NBO) analysis revealed that alkyne polarization controls partitioning between these cascades. A particularly remarkable transformation leads to the formation of *six* new bonds at the two alkyne carbons due to complete disassembly of the alkyne moiety and formal insertion of a nitrogen atom between the two acetylenic carbons of the reactant. This reaction offers a new synthetic approach for the preparation of polycyclic aromatic amides with a number of possible applications in molecular electronics. Another of the newly discovered cascades opens access to substituted analogues of *Sampangine* alkaloids which are known for their antifungal and antimycobacterial activity against AIDS-related opportunistic infection pathogens.

Introduction

Although alkynes are well-recognized as convenient building blocks for many useful transformations for organic synthesis, medicinal chemistry, and materials science,¹ their synthetic potential is far from being fully exploited. In particular, due to the possibility of facile formation of four new bonds at the expense of the two π -bonds, alkynes lend themselves to the

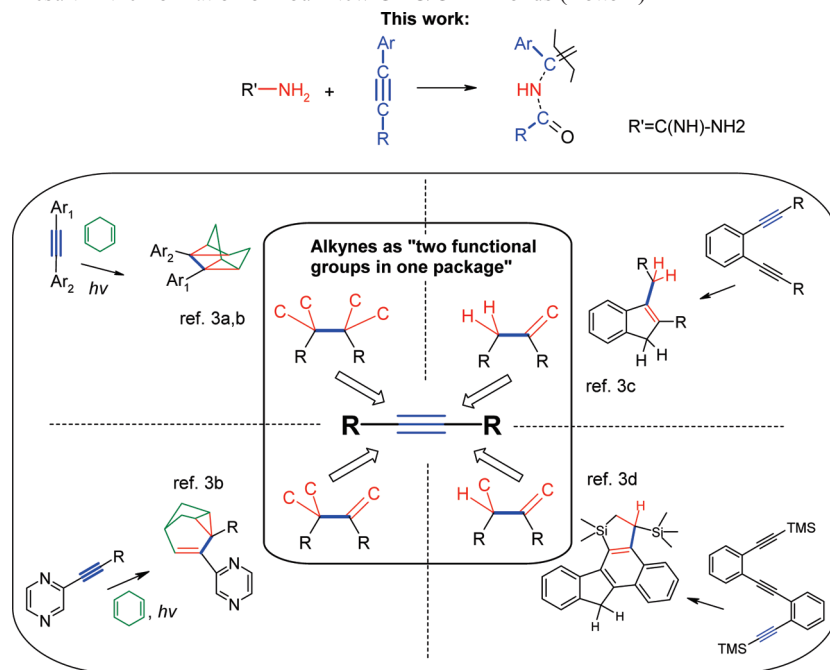
development of well-choreographed cascade transformations² which are impossible for their alkene “cousins” and in which the alkyne moiety behaves as two functional groups “in one

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SCHEME 1. Topological Analysis of the New Rearrangement/Fragmentation Reported in the Present Work (Top) and Selected Transformations of Alkynes Which Result in the Formation of Four New C–C/C–H Bonds (Bottom)



package". A number of recently reported cascade transformations shown in Scheme 1 illustrate this notion by showing how up to four new C–C and C–H bonds can be readily formed from a suitably positioned alkyne moiety.³ In this work, we wish to report an even more remarkable transformation that leads to the formation of *six* new bonds at the two alkyne carbons. This increase in the extent of structural changes is possible due to complete disassembly of the alkyne moiety and formal insertion of a nitrogen atom between the two acetylenic carbons of the reactant.

One of the most important questions in any addition to an unsaturated system is that of regioselectivity. This question translates into the problem of *endo/endo*selectivity if the addition proceeds through a cyclic transition state.⁴ Due to our long-standing interest in cyclizations of alkynes and interaction of the alkyne moiety with spatially close functional groups,⁵ we sought a deeper understanding of factors controlling such selectivity in cyclizations of alkynes through analysis of possible cyclization pathways in the system

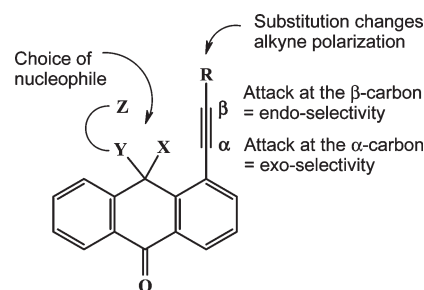


FIGURE 1. Factors responsible for the multichannel character of ring-closure reactions in adducts of peri-substituted acetylenyl-9,10-anthraquinones and guanidine.

shown in Figure 1. This system combines an activated alkyne moiety with a polyfunctional hemiaminal group derived from addition of guanidine to the carbonyl moiety of peri-substituted acetylenic anthraquinones **1a–c**. The presence of several nucleophilic and electrophilic centers in this group accounts for the multichannel mode of its interaction with the adjacent alkyne and several reaction cascades potentially originating from alternative cyclization modes. We will also show below that change in the nature of substituent R has the ability to control partitioning between these cascades through modulation of the polarization of the triple bond.

Whereas cyclizations of ortho-substituted aryl and hetaryl acetylenes are a well-recognized and efficient approach toward the preparation of annelated heterocyclic systems,⁶

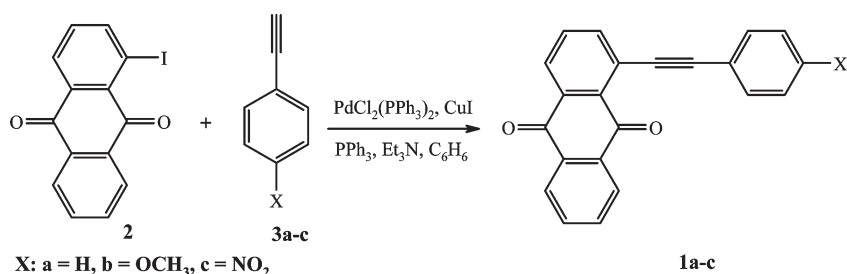
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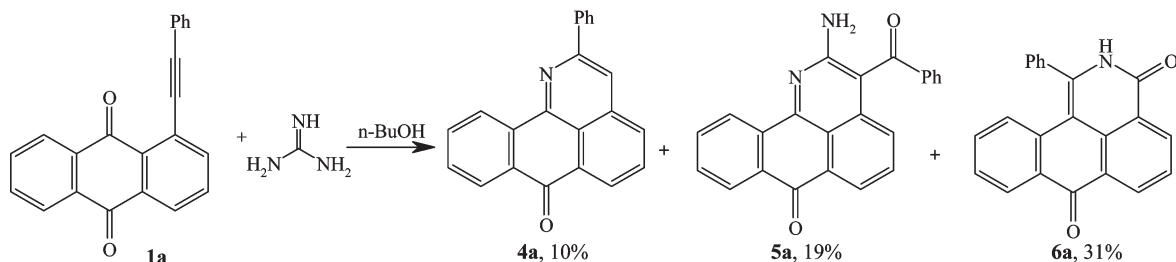
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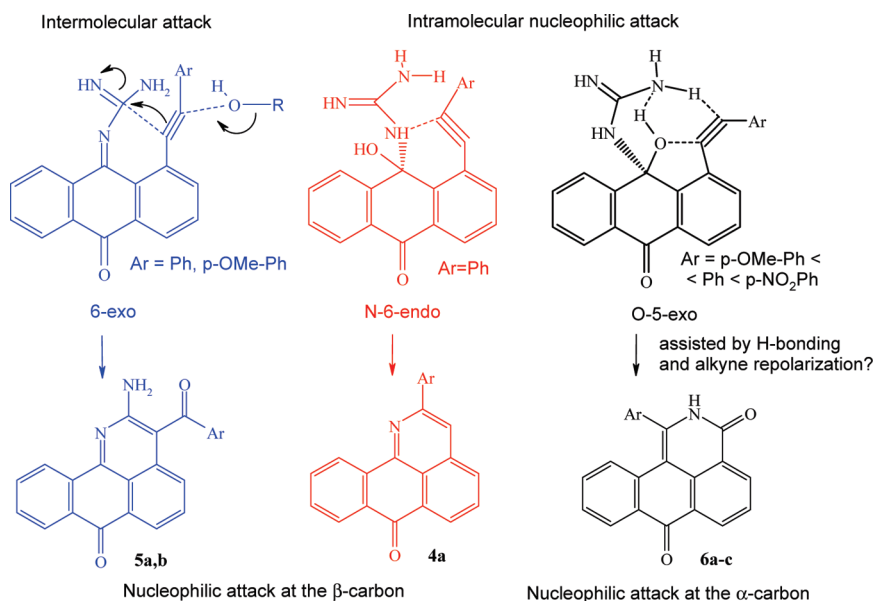
SCHEME 2. Synthesis of Starting Materials



SCHEME 3. Reaction of Acetylenic Quinone 1a with Guanidine



SCHEME 4. Diverging Mechanistic Pathways Accounting for the Three Observed Products



data on cyclization of peri-substituted acetylenyl-9,10-anthraquinones are limited to our earlier report of a new approach toward the synthesis of annelated heterocyclic systems based on the reaction of peri-substituted acetylenyl-9,10-anthraquinones and hydrazine.^{7b} A search for new cyclization types is important not only for the understanding of the general connection between structure and reactivity of organic compounds but also for expanding synthetic access to the condensed systems.

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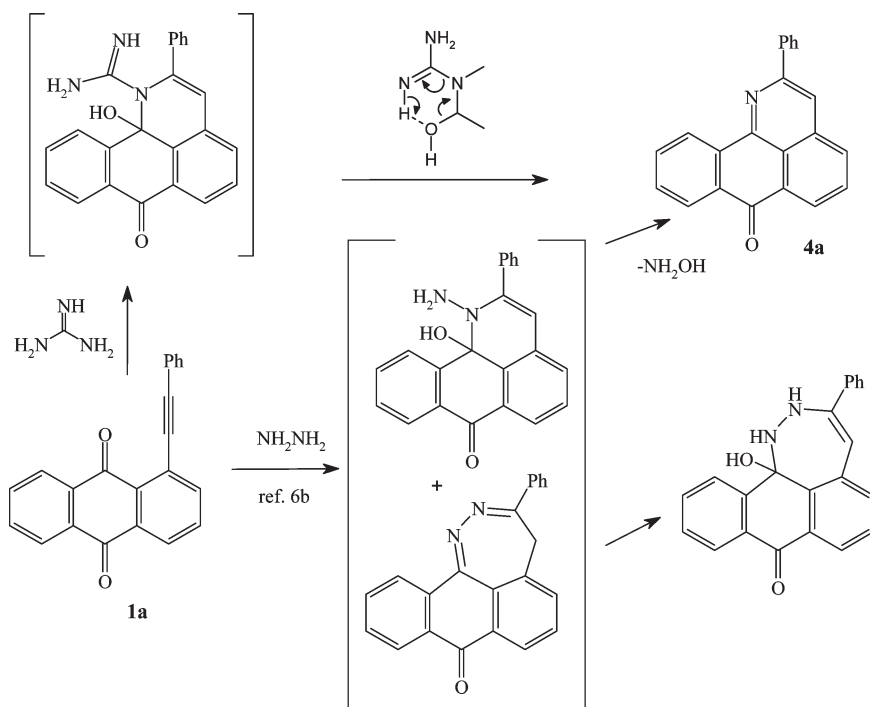
Results and Discussion

The starting materials, 1-ethynylaryl-9,10-anthraquinones **1a-c**, were prepared in 90–98% yields through Sonogashira cross-coupling⁸ of 1-iodo-9,10-anthraquinone **2** with phenylacetylene **3a**, p -methoxyacetylene **3b**, and p -nitrophenylacetylene **3c**, using the catalytic $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2\text{-CuI-PPh}_3\text{-Et}_3\text{N}$ system (Scheme 2).

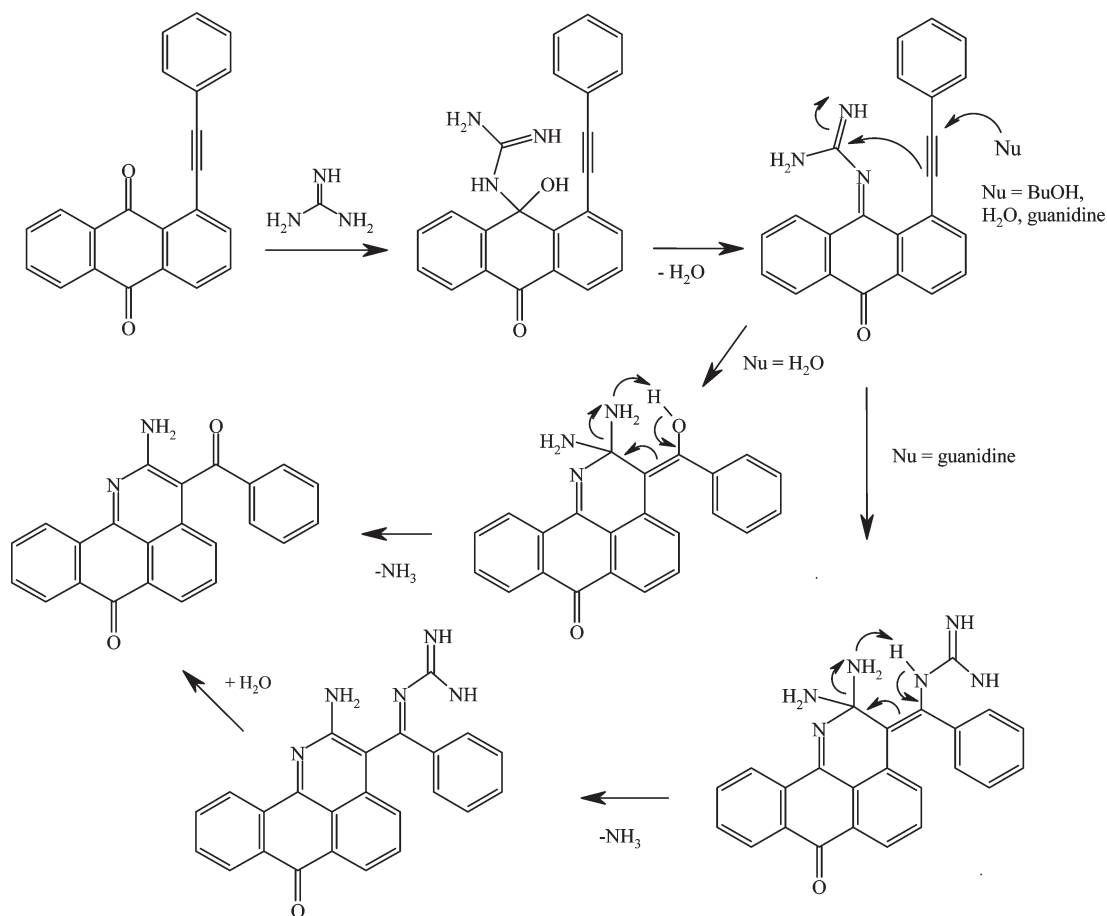
Interaction of guanidine with 1-phenylethynyl-9,10-anthraquinone **1a** in refluxing n -butanol proceeded with the

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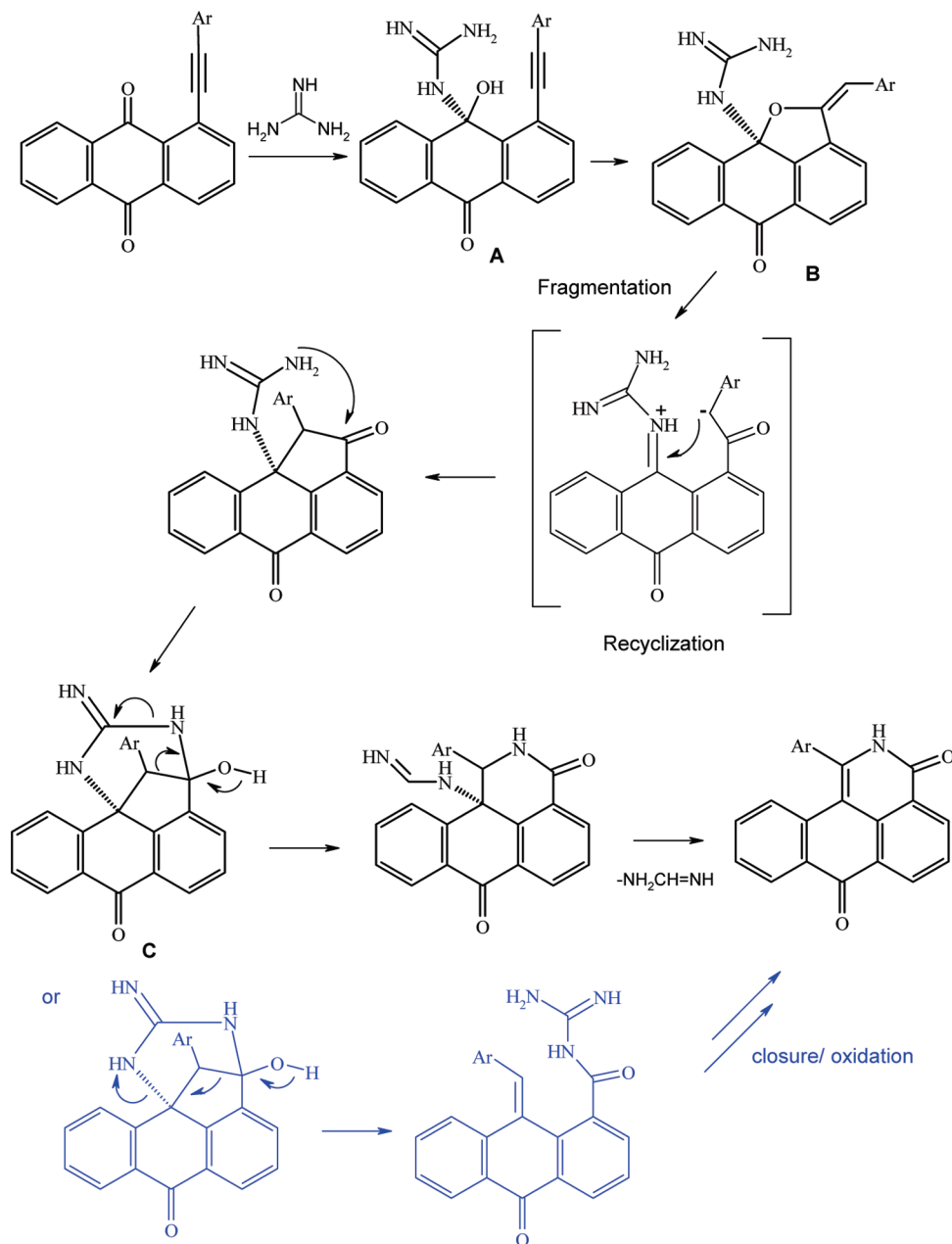
SCHEME 5. Suggested Mechanism for the Formation of Product 4a and Its Comparison with the Possible Mechanism for the Formation of 6-endo and 7-endo Products in the Earlier Reported Reaction of 1a with Hydrazine^{7b}



SCHEME 6. Suggested Mechanism for the Formation of Product 5a



SCHEME 7. Suggested Mechanism for the Formation of Products 6a–c



formation of three products **4a–6a** separated on silica gel (Scheme 3). Structures of the products were confirmed through a combination of 2D NMR techniques.

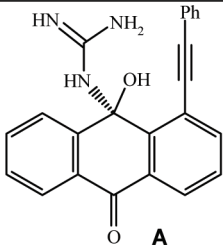
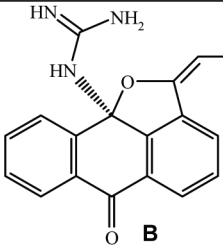
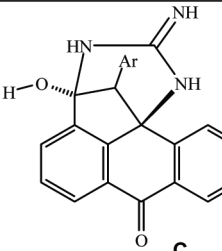
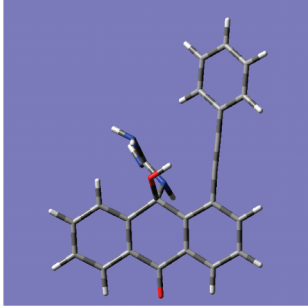


In particular, assignment of signals in ^1H and ^{13}C NMR spectra for compound **6a** in $\text{DMSO}-d_6$ has been accomplished via 2D NMR spectroscopy including $^1\text{H}-^1\text{H}$ correlation with double quantum filter (COSYDQF), inverse $^{13}\text{C}-^1\text{H}$ correlations of direct (HSQC) and long-range

(HMBC) $^{13}\text{C}-^1\text{H}$ couplings described in the SI. Because the sequence of cascade transformations leading to the formation of product **6a** was unexpected and interesting, we also investigated it through single-crystal X-ray analysis, which unambiguously confirmed the proposed 1-phenyl-7*H*-dibenzo[*de,h*]isoquinolin-3,7-dione structure (see the SI).⁹

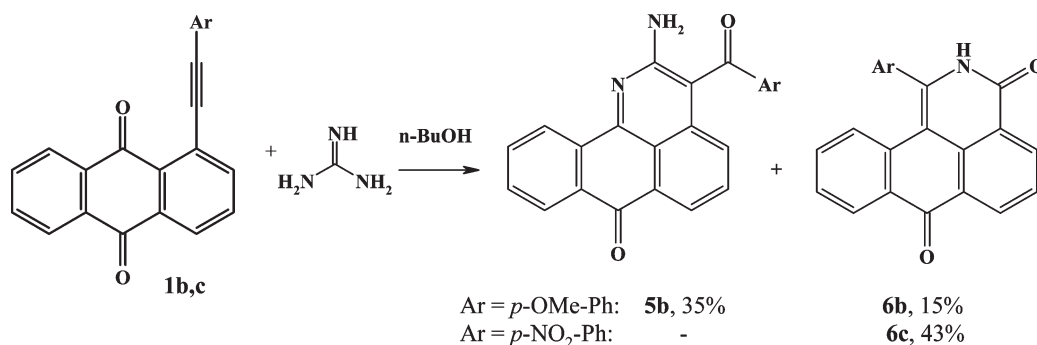
We suggest that formation of these products stems from three mechanistic pathways which diverge from a common intermediate (Scheme 4). Both the polarized triple bond of anthraquinone and the carbonyl groups present good targets for nucleophiles. Formation of the hemiacetal in the reaction of guanidine and the carbonyl moiety is likely to be fast but reversible and, thus, should result in a productive reaction pathway only when a subsequent exothermic step is available.

(9) Cambridge Structural Database (Cambridge, UK, version 5.29) has no information about the structure of compounds containing the 3*H*-dibenzo[*de,h*]isoquinolin-3,7(2*H*)dione moiety. The tetracyclic skeleton of compound **5** is folded along the C7–C11B line by 7.8°. Otherwise, the molecule is flat within ± 0.181 Å. The Ph group is rotated relative to the core by 70.4°. The centrosymmetric dimers in the crystal are organized through N2–H...O1 H-bonds (N–H 0.92(3), H...O 1.92(3) Å, N–H...O 175(2)°). Molecules in the crystal are organized in the herringbone packing with significant π -stacking interactions (the intermolecular distances of 3.54 Å).

TABLE 1. Optimized Geometries and Relative Energies of Selected Intermediates for the Formation of Product 6a at the B3LYP/6-31G(d,p) Level

Intermediate	 A	 B	 C
Optimized Geometry			
Relative Energy, in kcal/mol	0	-20.02	-27.04

SCHEME 8. Substituent Effect at the Competition between Two Cyclization Cascades



We believe that product **4a** is formed from the regioselective attack of hemiaminal nitrogen at the β -carbon of the alkyne.¹⁰ The 6-*endo*-dig selectivity for this closure is consistent with the triple bond polarization by the quinone moiety (vide infra). On the other hand, even though 5-*exo*-dig closures are often favored stereoelectronically relative to their 6-*endo*-dig counterparts,¹¹ the 5-*exo* attack of the oxygen nucleophile in this system proceeds against the triple bond polarization. An interesting possibility that underscores the polyfunctional character of the guanidine moiety is that presence of an appropriately positioned N–H bond near the developing negative center in the 5-*exo*-dig transition state (Scheme 4, top right) may provide an

additional factor in favor of such a pathway. This hypothesis is consistent with the absence of 5-*exo*-attack of the nitrogen atom, where such assistance is impossible, and with the observation that the reaction of quinone **1a** with a nitrogen nucleophile is incapable of such assistance (hydrazine) does not provide any products derived from this path.⁷ This observation also suggests that the competition between the *N*-6-*endo* and *O*-5-*exo*-products **4a** and **6a** may be fine-tuned through the change in the triple bond polarization (vide infra). Finally, the minor product is consistent with an *external* nucleophilic attack at the electron-deficient end of the polarized triple bond with concomitant trapping of the developing carbon nucleophile with the C=N moiety of guanidine in a 6-*endo*-dig manner.

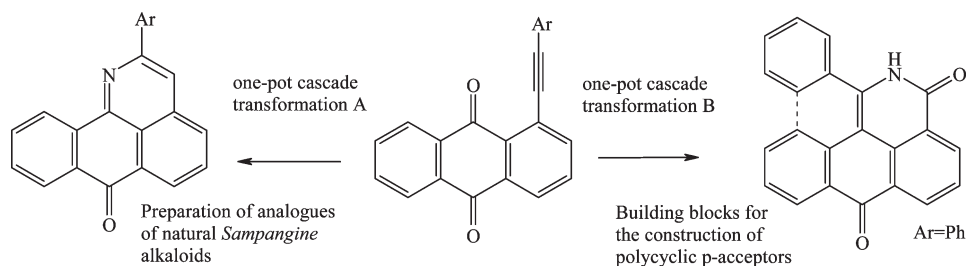
Formation of phenyl-7*H*-dibenzo[*de,h*]quinolin-7-one **4a** can be rationalized through consecutive addition of a guanidinium amino group at the carbonyl carbons and the triple bond (in a 6-*endo* fashion) with the subsequent elimination of water and NH₂CN (or hydroxylamine and HCN).

(10) At this point, we cannot exclude an alternative mechanism that includes initial attack of guanidine at the triple bond followed by cyclization of the intermediate on the carbonyl. Note, however, that the positive charge is significantly larger at the carbonyl carbon than it is at either of the two carbons of the alkyne moiety (Table 2).

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TABLE 2. Natural Bond Orbital (NBO)¹⁴ Analysis of Substituent Effects on Polarization of the Triple Bond and the Adjacent Carbonyl Group in Anthraquinones **1a–c** at the B3LYP/6-31G(d,p) Level¹⁵

	<i>p</i> -OMe-Ph, 1b	Ph, 1a	<i>p</i> -NO ₂ Ph, 1c
π_{in} , population	1.965	1.966	1.966
π_{in}^* , polarization (% at β -carbon)	49.19	49.38	49.13
π_{out} , population	1.839	1.840	1.834
π_{out}^* , polarization (% at β -carbon)	52.53	51.99	50.65
π_{CO} , population	1.955	1.955	1.955
π_{CO}^* , polarization (% at carbon)	66.27	66.24	66.29
charges C(O)/C α /C β	0.538/−0.004/0.044	0.540/0.004/0.042	0.542/0.035/0.023

SCHEME 9. Summary of Synthetic Opportunities Offered by the New Cascade Transformations

The 6-*endo*-closure is similar to that observed earlier in the reaction of **1a** with hydrazine^{7b} (Scheme 5).

Formation of 2-amino-3-benzoyl-7*H*-dibenzo[*de,h*]quinoxalin-7-one **5a** can be described through several mechanisms, the shortest of which is given in Scheme 6. The key step in the proposed sequence is nucleophilic attack at the remote acetylenic carbon with concomitant trapping of the developing vinyl anion by the internal C=NH electrophile in the 6-*exo* fashion. The incoming nucleophile may be guanidine, butanol (the solvent), or water produced in the previous step of the reaction cascade. Transformation of the cyclized intermediate in the final product is accompanied by aromatization, which should provide the driving force for the C–N bond cleavage that furnishes compound **5a**.

However, formation of the rearranged product **6a** was rather unusual and should result from a cascade transformation that follows addition, cyclization, rearrangement, and elimination of guanidine fragments. The exact mechanism for the formation of isoquinoline-3,7-dione **6a** is yet unknown. A possible sequence of steps outlined in Scheme 7 involves the 5-*exo*-dig closure followed by a fragmentation–recyclization sequence that resembles the retro-aldolization–aldol condensation sequence of the Fujimoto–Belleau reaction¹² and the Petasis–Ferrier rearrangement.¹³

We tested the feasibility of several intermediates involved in this mechanism by calculating their relative energies at the B3LYP/6-31G(d,p) level. Results summarized in Table 1 suggest that indeed the products of 5-*exo* cyclization

and the fragmentation/recyclization sequences **B** and **C** lie respectively ca. 20 and 27 kcal/mol lower in energy than the first hemiaminal intermediate **A**.

To test the importance of triple bond polarization in this mechanism, we expanded the list of substrates and investigated the reactivity of *p*-nitro- and *p*-methoxy-substituted acetylenes **1b** and **1c**. The presence of an acceptor nitro group at the terminal aromatic ring increases the yield for the unusual products **6** by almost 50%. This observation further supports the notion that this mechanistic path starts with 5-*exo*-dig nucleophilic attack at the α -carbon. Interestingly, interaction of nitroacetylene **1c** also led to the formation of a small amount (~14%) of 1-(*p*-aminophenylethynyl)-9,10-anthraquinone **7**, the product of the nitro-group reduction. On the contrary, the presence of a donor methoxy group had the opposite effect, favoring external nucleophilic attack at the terminal carbon and the formation of compound **5b** at the expense of compounds **4** and, to some extent, **6** (Scheme 8).

These results are consistent with the analysis of acetylenic π -bonds polarization by the Natural Bond Orbital (NBO) analysis. These results summarized in Table 2^{14,15} show that the presence of the donor substituent increases the out-of-plane π -density at the α -carbon of the triple bond, whereas the electron acceptor nitro group has the opposite effect. In contrast, both the in-plane π -bond and the adjacent carbonyl moiety show very little perturbation by the substituents.

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Conclusion

In summary, we have illustrated the possibility of multiple reaction pathways originating from the reaction of a polarized triple bond with the appropriately positioned multifunctional hemiaminal moiety. The most remarkable of these reactions leads to the formal cleavage of the triple bond and insertion of one of the guanidine nitrogen atoms between the two acetylenic carbons. Although further work is needed to fully understand the mechanistic subtleties involved in this process, it is clear that, besides its uniqueness from the conceptual point of view, this chemistry also offers a new synthetic approach for the preparation of polycyclic aromatic amides.

In particular, one of these cascades opens access to substituted analogues of *Sampangine* alkaloids which are known for their antifungal and antimycobacterial activity against AIDS-related opportunistic infection pathogens¹⁶ whereas the other cascade, which leads to the formal transposition of N and C atoms, leads to molecules which may be useful as a structural element for hydrophobic dimerizations¹⁷ as well as for the construction of systems for fundamental studies of electron and energy transfer phenomena,¹⁸ design of photovoltaic devices, organic field effect transistors, and light emitting diodes (Scheme 9).^{19,20}

Experimental Section

General Procedure for Reaction of 1-Acetylenyl-9,10-anthraquinones with Guanidine. A mixture of guanidine (19.5 mmol, 19.5 mL of 1 M solution in methanol) and the respective anthraquinone **1a–c** (3.25 mmol) was refluxed in 50 mL of butanol-1 for 18–20 h. Under these conditions, the amount of unreacted 1-acetylenylantraquinones is about 20–35%. Longer heating leads to partial thermal decomposition and complicates isolation and purification of reaction products. Solvent was evaporated in vacuo. The mixture was purified by column chromatography on silica gel ($d = 25$ mm, $h = 170$ mm, elution with benzene followed by ethyl acetate). Subsequent recrystallization gave pure compounds **4–7**.

For **1a**, the yield of phenyl-7*H*-dibenzo[*de,h*]quinolin-7-one **4a** is 70 mg (10%), mp 207.5–208.5 °C (from benzene),

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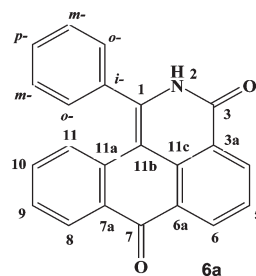
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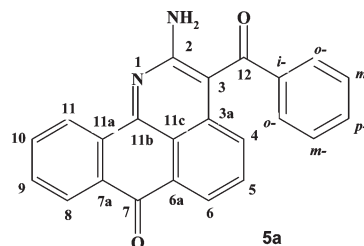
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lit. mp 207–208 °C. All spectral data are analogous to literature data.²¹



The yield of 1-phenyl-7*H*-dibenzo[*de,h*]isoquinolin-3,7-dione **6a** is 200 mg (31%), mp > 360 °C (from 1,4-dioxane). IR (cm^{-1}) ν 1648, 1670 (C=O), 3055 (NH); ¹H NMR ((CD₃)₂SO, 300 MHz) δ 12.08 (s, 1H, NH), 8.70–8.65 (m, 2H, H-4, H-6), 8.25 (dd, $J = 1.2, 7.8$ Hz, 1H, H-8), 7.86 (t, $J = 7.7$ Hz, 1H, H-5), 7.65–7.55 (m, 5H, Ph), 7.35 (t, $J = 7.8$ Hz, 1H, H-9), 7.23–7.17 (m, 1H, H-10), 6.81 (d, $J = 8.3$ Hz, 1H, H-11); ¹³C NMR ((CD₃)₂SO, 100 MHz) δ 181.7 (C-7), 160.9 (C-3), 145.8 (C-1), 135.1 (C-11a), 134.6 (C-11c), 135.5 (C_i), 132.9 (C-6), 132.6 (C-4), 131.8 (C-10), 130.3 (C_p), 129.9 (C-7a), 129.5 (C_o), 129.3 (C_m), 127.5 (C-6a), 127.1 (C-8), 127.0 (C-5), 127.0 (C-9), 126.4 (C-11), 124.7 (C-3a), 104.1 (C-11b); HRMS calcd for C₂₂H₁₃NO₂ 323.0946, found 323.0946.



The yield of 2-amino-3-benzoyl-7*H*-dibenzo[*de,h*]quinolin-7-one **5a** is 130 mg (19%), mp 201–201.3 °C (from benzene). IR (cm^{-1}) ν 1634, 1667 (C=O), 3368, 3492 (NH₂); ¹H NMR (CDCl₃, 400 MHz) δ 8.81 (dd, $J = 1.2, 7.8$ Hz, 1H, H-11), 8.37 (dd, $J = 1.2, 7.8$ Hz, 1H, H-8), 8.24 (dd, $J = 1.2, 7.0$ Hz, 1H, H-6), 7.77 (td, $J = 1.36, 7.8$ Hz, 1H, H-10), 7.72–7.69 (m, 2H, H_o), 7.66 (td, $J = 1.36, 7.8$ Hz, 1H, H-9), 7.59–7.54 (m, 1H, H_p), 7.52 (dd, $J = 1.2, 8.6$ Hz, 1H, H-4), 7.47–7.39 (m, 3H, H-5, H_m), 5.95 (s, 2H, NH₂); ¹³C NMR (CDCl₃, 100 MHz) δ 197.1 (C-12), 183.3 (C-7), 155.1 (C-2), 151.1 (C-11b), 139.8 (C_i), 136.5 (C-6a), 135.5 (C-11a), 133.7 (C-10), 133.1 (C_p), 132.5 (C-7a), 131.0 (C-9), 130.7 (C-4), 130.4 (C-5), 129.4 (C_o), 129.0 (C-3a), 128.7 (C_m), 127.4 (C-8), 125.6 (C-6), 125.4 (C-11), 117.7 (C-11c), 106.1 (C-3); HRMS calcd for C₂₃H₁₄N₂O₂ 350.1055, found 350.1055.

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Supporting Information Available: Yields and experimental conditions for the cyclizations, synthesis of starting materials, ¹H and ¹³C NMR spectra, details of X-ray crystallographic analysis, energies, and geometries for reactants and intermediates calculated at the B3LYP/6-31G(dp) level. This material is available free of charge via the Internet at <http://pubs.acs.org>.