Novel Intramolecular [4 + 2] Cycloaddition Reactions of Enamines and Enamides with Unactivated Dienes[1]

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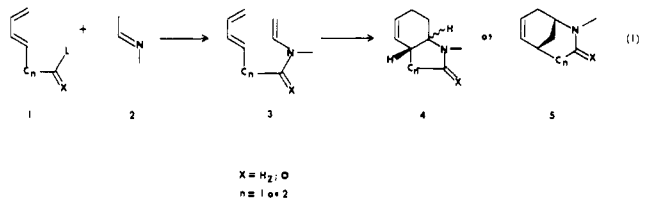
Abstract: During the course of a broad investigation of the intramolecular [4 + 2] cycloaddition reactions of enamines and enamides with unactivated butadienes, efforts were directed toward the construction of the spirocycles **10a** and **10b** which possess the molecular framework characteristic of the *Erythrina* alkaloids. Whereas it was not possible to prepare the requisite enamino diene **9a** or the enamido diene **9b** by the reaction of 1-methyl-3,4-dihydroisoquinoline (**8**) with 3,5-hexadienyl triflate (**6**) or 3,5-hexadienoyl chloride (**7**), the enamine **16a** and the enamide **16b**, in which the dienoic moiety is expeditiously masked as a sulfolene derivative, were readily produced upon coupling **8** with the triflate **14b** or the acid chloride **15b**. Interestingly, thermolysis of **16a** or **16b** in refluxing xylene did not afford the expected spirocycles **10a** and **10b** but rather the bridged cycloadducts **17a** and **17b**, respectively. Moreover, thermolysis of the enamide **16b** for only 3.5 min in refluxing xylene produced a mixture of the enamido diene **9b** and the vinylcyclobutane **21b** together with recovered starting material. When either the enamido diene **9b** or the enamide **16b** was heated at reflux in xylene for 15 min, the vinylcyclobutane **21b** was obtained in virtually quantitative yield. The vinylcyclobutane **21b** underwent facile thermal rearrangement to the 2-azabicyclo[3.3.1]nonene **17b**. On the other hand, hydride reduction of **21b** followed by thermolysis of the intermediate amino vinylcyclobutane **21a** afforded **17a**. Thus, the latent enamino diene **16a** and enamido diene **16b** appear to extrude sulfur dioxide to form **9a** and **9b**, which then undergo a remarkably facile, intramolecular thermal [2 + 2] cycloaddition, probably via the diradicals **20a,b**, to afford the vinylcyclobutanes **21a,b**. Continued thermolysis of **21a,b** results in their smooth rearrangement to the more stable bridged [4 + 2] cycloadducts **17a,b**. Although the regiochemical course of these intramolecular [4 + 2] cycloadditions was unpredicted, these observations are significant in that they appear to represent the first examples of a cycloaddition reaction of enamine and enamide with an unactivated butadiene.

As an integral part of a general program directed toward the design and development of new strategies for the synthesis of nitrogen-containing natural products, we initiated a series of investigations to probe the feasibility of employing intramolecular [4 + 2] cycloaddition reactions[2] of nitrogen-substituted dienophiles **3** for the construction of functionalized hydroindoles **4** (n = 1) and hydroquinolines **4** (n = 2) (eq 1), which are structural ele-



(1)

ments common to a diverse array of alkaloids. An important feature of this novel approach to these heterocyclic synthons is the particular facility with which the intermediate enamino dienes **3** (X = H_2) and the enamido dienes **3** (X = O) may be assembled employing a carbon–nitrogen bond forming reaction to couple the dienoic and dienophilic moieties. For example, N-alkylation of the imine **2** with an alkylating agent **1** (X = H_2; L = OTs, I, OTf, etc.) followed by deprotonation of the intermediate iminium salt would produce the enamino diene **3** (X = H_2), whereas N-acylation of the imine **2** with an acid chloride **1** (X = O; L = Cl) would afford the enamido diene **3** (X = O). Although prior to the commencement of these investigations the general synthetic utility of the bimolecular[3] and intramolecular[4] [4 + 2] cycloaddition reactions of dienamides had been firmly established, neither the bimolecular nor the intramolecular [4 + 2] cycloaddition reactions of enamines or enamides with *unactivated* dienes had been reported.[5] Indeed reports of the [4 + 2] cycloaddition reactions of electron-rich dienophiles with unactivated dienes are rare[6-8] and appear to represent special cases rather than general examples. While the donor–acceptor properties of the dienophilic and dienoic moieties of the enamino diene **3** (X = H_2) and the enamido diene **3** (X = O) are not complementary, the highly favorable entropic assistance that is inherent in intramolecular processes seemed to auger well for the successful intramolecular [4 + 2] cycloaddition reaction of substrates related to **3**.

In addition to the fundamental issue of whether the intramolecular cycloaddition of an enamine or enamide with an unactivated diene is feasible, there are also important questions regarding the regiochemical and stereochemical outcome of these reactions. Based upon a survey of the literature,[2] it is readily apparent that a variety of substrates structurally related to **3** (n = 1 or 2), wherein the internal double bond of the diene moiety is trans, exhibit a pronounced tendency to undergo intramolecular [4 + 2] cycloaddition reactions to form fused bicyclic systems rather than bridged bicyclic ones. The transition state for the formation of a bridged bicyclic system in these reactions is presumably more highly strained relative to the alternate pathway that would lead to a fused ring system. In contrast to existing examples, however, the dienophile of **3** is an electron-rich enamine or enamide and the diene is unactivated, and, when *only* primary orbital interactions are considered, FMO calculations suggest that meta products should be produced by the [4 + 2] cycloaddition reaction

(1) For a preliminary account of portions of this work see: Martin, S. F.; Chou, T.; Tu, C. *Tetrahedron Lett.* **1979**, 3823.
(2) For a review see: Oppolzer, W. *Angew Chem., Int. Ed. Engl.* **1977**, *16*, 10.
(3) (a) Overman, L. E.; Jessup, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 5179, and references cited therein. (b) Mariano, P. S.; Huesmann, P. L.; Beamer, R. L.; Dunaway-Mariano, D. *Tetrahedron* **1978**, *34*, 2617.
(4) (a) Oppolzer, W. *J. Am. Chem. Soc.* **1971**, *93*, 3834. (b) Oppolzer, W.; Fröstl, W. *Helv. Chim. Acta* **1975**, *58*, 590. (c) Oppolzer, W.; Fröstl, W.; Weber, H. P. *Ibid.* **1975**, *58*, 593. (d) Stork, G.; Morgans, Jr., D. J. *J. Am. Chem. Soc.* **1979**, *101*, 7110.
(5) The bimolecular cycloaddition of enamines with electron-deficient dienes is, however, known. See, inter alia, (a) Bohlmann, F.; Habeck, D.; Poetsch, E.; Schumann, D. *Chem. Ber.* **1967**, *100*, 2742. (b) Danishefsky, S.; Cavanaugh, R. *J. Org. Chem.* **1968**, *33*, 2959. (c) Evans, D. A.; Bryan, C. A.; Sims, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 2891. (d) Bohlmann, F.; Mueller, H. J.; Schumann, D. *Chem. Ber.* **1973**, *106*, 3026. (e) Dauben, W. G.; Kozikowski, A. P. *J. Am. Chem. Soc.* **1974**, *96*, 3664.
(6) For a cycloaddition reaction between a metallo enamine and isoprene see: Takabe, K.; Fujiwara, H.; Katagiri, T.; Tanaka, J. *Tetrahedron Lett.* **1975**, 1239.
(7) For a cycloaddition reaction between an enol ether and *o*-quinodimethanes see: Fleming, I.; Gianni, F. L.; Mah, T. *Tetrahedron Lett.* **1976**, 881.
(8) For a report of the Fe(0)-catalyzed cycloaddition of an ynamine and butadiene see: Genet, J. P.; Ficini, J. *Tetrahedron Lett.* **1979**, 1499.

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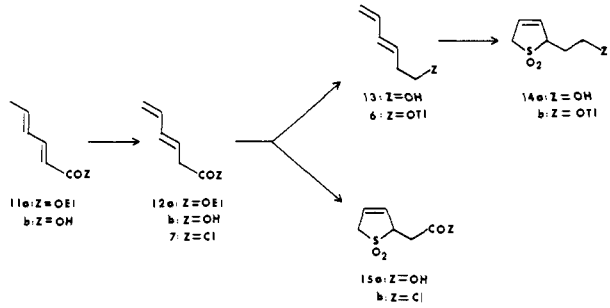
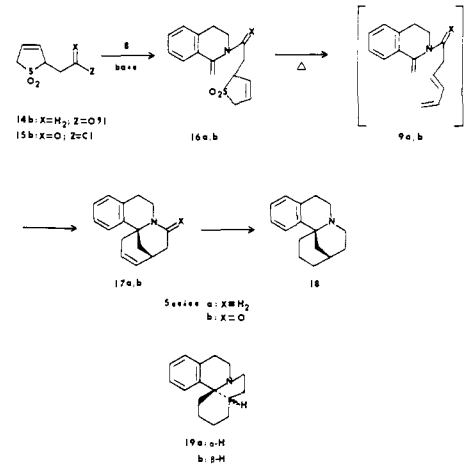
Scheme I



Scheme II

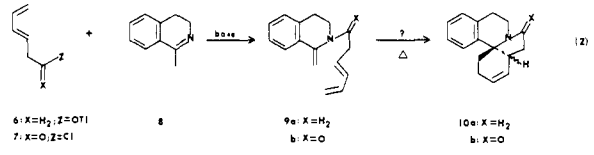


of such substances.[9] If electronic effects were dominant in these intramolecular processes, one might then reasonably expect that the formation of bridged bicyclic systems **5** would be favored, but, given the established importance of the geometrical and conformational constraints characteristic of intramolecular reactions, the regiochemical course of the cycloadditions of **3** (n = 1 or 2) to give the fused products **4** (n = 1 or 2) still seemed to be on relatively firm grounds. Since the stereochemical outcome of intramolecular [4 + 2] cycloaddition reactions of compounds related to **3** (n = 1 or 2) is determined by the subtle differences in the transition-state energies for each of the possible spatial orientations of the dienophile and the diene, any prediction of the preferred formation of cis- or trans-fused products **4** seemed unjustified. Indeed, cis- and/or trans-fused bicyclo[4.3.0] and -[4.4.0] ring systems may be produced in these cycloadditions.[4,10,11]

We have recently discovered that the intramolecular [4 + 2] cycloaddition reactions of enamines and enamides with unactivated dienes may lead to the formation of bridged[1] or fused[11] cycloadducts. We now wish to report the details of our studies directed toward the elucidation of the important pathways operating in those cases wherein bridged cycloadducts are produced.

Results and Discussion

Our initial studies to assess the feasibility of employing intramolecular [4 + 2] cycloadditions of enamines and enamides with unactivated dienes for the construction of hydroindole ring systems were directed toward attempts to elaborate the tetracyclic spiroamine **10a** and the spiroamide **10b**, which possess the unusual molecular framework characteristic of the *Erythrina* alkaloids (eq 2). On the basis of precedent in the literature,[5a] it seemed



(2)

eminently reasonable that the N-alkylation or N-acylation of 1-methyl-3,4-dihydroisoquinoline (**8**)[12] with the triflate **6** or the acid chloride **7** in the presence of base should afford the key intermediate enamino diene **9a** or the enamido diene **9b**, respectively. The preparation of the requisite dienoic alkylating and acylating agents **6** and **7** was therefore undertaken. 3,5-Hexadienol (**13**) had been previously prepared by the hydride reduction of 3,5-hexadienoic acid (**12b**),[13] but the reported procedure for the preparation of **12b** by the reaction of carbon dioxide with pentadienyl anion was not considered practical for large-scale application,[14] and consequently an alternate route to the dienol **13** was developed (Scheme I). Thus, deprotonation of ethyl sorbate (**11a**) using the 1:1 complex of lithium diisopropylamide (LDA) and hexamethylphosphoramide (HMPA) at −78 °C followed by kinetic protonation of the intermediate trienolate with aqueous acetic acid afforded the deconjugated ester **12a** in 88% yield.[15] The subsequent reduction of **12a** with lithium aluminum hydride provided the alcohol **13** in 92% yield. Although the crude triflate **6** could then be conveniently prepared by the reaction of the dienol **13** with freshly distilled triflic anhydride,[16] several attempts to couple **6** with the dihydroisoquinoline **8** did not lead to the formation of detectable amounts of the enamino diene **9a**. The known tosylate[13] derived from **13** also failed to react with **8** under a variety of reaction conditions. Hoping that the preparation of the enamido diene **9b** might prove a more successful venture, we prepared the acid chloride **7** in 84% overall yield by deconjugation of sorbic acid **11b** (LDA/THF, −10 °C)[17] followed by reaction of the intermediate 3,5-hexadienoic acid (**12b**) with thionyl chloride in benzene. However, the reaction of the dihydroisoquinoline **8** with **7** did not produce appreciable quantities of the requisite enamido diene **9b**.

Since there was adequate precedent for the alkylation and acylation of the dihydroisoquinoline **8** with simple electrophilic partners to give enamines and enamides,[5a] it appeared likely that the presence of the conjugated diene moiety itself was the source of the difficulties. Consequently, an alternate approach to the syntheses of **9a** and **9b** was devised that entailed the preparation of the enamine **16a** and the enamide **16b** in which the diene unit is expeditiously masked as a 2-alkyl-2,5-dihydrothiophene 1,1-dioxide (Scheme II).[18] Thus, dissolution of 3,5-hexadienol (**13**) in liquid sulfur dioxide containing hydroquinone at room temperature produced the cycloadduct **14a** (85%). Subsequent treatment of **14a** with freshly prepared triflic anhydride[16] in the presence of anhydrous potassium carbonate afforded the unstable triflate **14b**, which was allowed to react in situ with the dihydroisoquinoline **8**. The latent enamino diene **16a** thus produced was, without isolation, thermolyzed in refluxing xylene (8 h) to give a cycloadduct in 36% overall yield from the dihydroiso-

(9) We wish to thank Mr. R. David Mitchell (University of Texas, Austin) for these calculations. See also ref 7.

(10) Inter alia see: (a) House, H. O.; Cronin, T. *J. Org. Chem.* **1965**, *30*, 1061. (b) Gschwend, H. W.; Lee, A. O.; Meier, H.-P. *Ibid.* **1973**, *38*, 2169. (c) Gschwend, H. W. *Helv. Chim. Acta* **1973**, *56*, 1763. (d) Bajorek, J. J. S.; Sutherland, J. K. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1559. (e) Oppolzer, W.; Snowden, R. L. *Tetrahedron Lett.* **1976**, 4187. (f) Oppolzer, W.; Fehr, C.; Warneke, J. *Helv. Chim. Acta* **1977**, *60*, 48. (g) Roush, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 3599. (h) Wilson, S. R.; Mao, D. T. *Ibid.* **1978**, *100*, 6289. (i) Näf, F.; Decorzant, R.; Thommen, *W. Helv. Chim. Acta* **1979**, *62*, 114. (j) Taber, D. F.; Gunn, B. P. *J. Am. Chem. Soc.* **1979**, *101*, 3992.

(11) Martin, S. F.; Desai, S. R.; Phillips, G. W.; Miller, A. C. *J. Am. Chem. Soc.*, **1980**, *102*, 3294.

(12) Thesing, J.; Funk, F. H. *Chem. Ber.* **1958**, *91*, 1546.

(13) Howden, M. E. H.; Maercker, A.; Burdon, J.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 1732.

(14) Paul, R.; Tchelitcheff, S. *Bull. Soc. Chim. Fr.* **1948**, 108.

(15) For a closely related reaction see: Stevens, R. V.; Cherpeck, R. E.; Harrison, B. L.; Lai, J.; Lapalme, R. *J. Am. Chem. Soc.* **1976**, *98*, 6317.

(16) Burdon, J.; Farazmand, I.; Stacey, M.; Tatlow, J. C. *J. Chem. Soc.* **1957**, 2574.

(17) Cf. Pfeffer, P. E.; Silbert, L. S. *J. Org. Chem.* **1971**, *36*, 3290.

(18) For other recent examples in which a 2,5-dihydrothiophene 1,1-dioxide serves as a latent 1,3-diene see: (a) Inomata, K.; Kinoshita, H.; Takemoto, H.; Murata, Y.; Kotake, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3341. (b) Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208. (c) McIntosh, J. M.; Sieler, R. A. *Ibid.* **1978**, *43*, 4431. (d) Nicolaou, K. C.; Barnette, W. E.; Ma, P. *J. Org. Chem.* **1980**, *45*, 1463. (e) Oppolzer, W.; Roberts, D. A.; Bird, T. G. C. *Helv. Chim. Acta* **1979**, *62*, 2017.

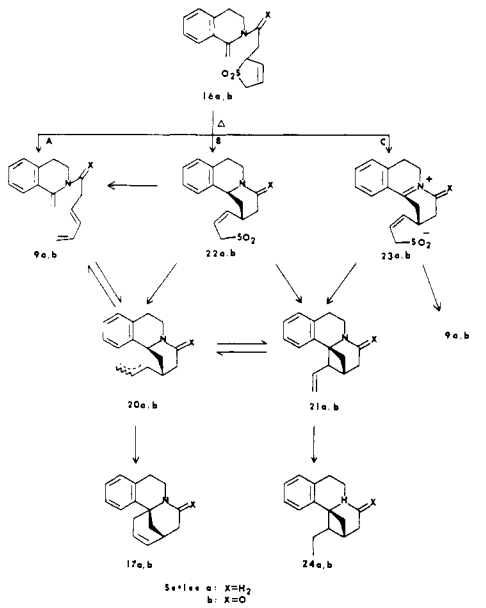
quinoline **8**, presumably via the enamino diene **9a**. Although the product of this cycloaddition reaction was initially thought to be the desired spiroamine **10a**, such optimism was soon dispelled by the observation that catalytic hydrogenation (H_2/10% Pt–C/AcOH) of this compound did not provide either of the known erythrinanes **19a** or **19b**.[19] Based upon an examination of the NMR and IR data, it seemed probable that the cycloadduct was the unexpected 2-azabicyclo[3.3.1]nonene **17a**. In order to confirm this suspicion, a single-crystal X-ray analysis of the hydrobromide salt of the dihydro derivative of this cycloadduct was performed which unequivocally established its structure as being the unusual 2-azabicyclo[3.3.1]nonane **18**.[20] Thus, the product of the intramolecular [4 + 2] cycloaddition was most probably the bridged cycloadduct **17a**.

Thinking somewhat naively that the enamido diene **9b**, wherein the dienophile is less electron rich than in the enamine **9a**, might undergo an intramolecular [4 + 2] cycloaddition in the desired regiochemical sense, we then directed efforts toward the synthesis of the masked enamido diene **16b**. In the event, the reaction of 3,5-hexadienoic acid (**12b**) with excess sulfur dioxide in the presence of hydroquinone at 40 °C afforded the 2-substituted dihydrothiophene dioxide **15a** (71%). Subsequent treatment of the acid **15a** with thionyl chloride in dichloromethane produced the acid chloride **15b** which coupled smoothly with the dihydroisoquinoline **8** in the presence of triethylamine to give the latent enamido diene **16b** in 67% overall yield. Upon thermolysis of **16b** in refluxing xylene (7 h), the initial extrusion of sulfur dioxide produced the intermediate enamido diene **9b**, which then readily underwent a subsequent intramolecular cycloaddition to give a [4 + 2] cycloadduct in 97% yield. However, that this new cycloadduct was the 2-azabicyclo[3.3.1]nonene **17b** was easily demonstrated by its facile transformation via hydride reduction to the amine **17a**, the same product obtained from the previous thermolysis of **16a**.

The remarkable and surprising regiochemical course of these intramolecular [4 + 2] cycloaddition reactions is not yet fully understood. When the diene moiety is unmasked by the cheletropic expulsion of sulfur dioxide from **16a** or **16b**, the trans enamino diene **9a** or the trans enamido diene **9b**, respectively, should be formed. This presumption is made not only upon literature precedent,[21] but also on the experimental observation that the thermolysis of **14a** in xylene produced 3(*E*),5-hexadien-1-ol (**13**) with a high degree (>90%) of stereoselectivity. Furthermore, brief thermolysis of the enamide **16b** in refluxing xylene afforded **16b** together with small amounts of an enamido diene (vide infra) which, based upon the ^1H NMR, appears to be predominantly the trans isomer **9b**, but the possibility that traces of the corresponding cis enamido diene were also formed in this reaction could not be rigorously excluded. Several attempts to isolate the trans enamino diene **9a** from the thermolysis of the enamine **16a** were unsuccessful. Since the trans → cis isomerization of the diene moiety under these reaction conditions seems unlikely, it is reasonable to assume that **9a** and **9b** are intermediates that undergo the intramolecular cycloaddition reaction.

Based upon an inspection of molecular models, the transition state for a "concerted" intramolecular [4 + 2] cycloaddition reaction from **9a** and **9b** to give the bridged cycloadducts **17a** and **17b**, respectively, appears to be highly strained.[22] Speculation that the conversion **16a,b** → **17a,b** proceeded by a sequence of reactions in which the two new carbon–carbon bonds produced by the cycloaddition were formed in a stepwise manner[23-25] seemed

Scheme III



warranted, and several such mechanistic possibilities are outlined in Scheme III. If one initially assumes that the enamino diene **9a** and the enamido diene **9b** are the intermediates (path A), a two-step process for the cycloaddition is not surprising owing to the poor donor–acceptor electronic characteristics of the dienophile and the diene. The formation of **10a** and **10b** might still be predicted on the basis of the relative electronic stability of the various intermediate diradicals, but steric and/or conformational factors appear to favor the kinetic production of diradicals such as **20a** and **20b**. Collapse of the diradicals **20a,b** could then afford either the vinylcyclobutanes **21a,b** or the 2-azabicyclo[3.3.1]-nonenes **17a,b**, depending upon the geometry of the allylic radical. Although the cheletropic extrusion of sulfur dioxide from simple 2-substituted 2,5-dihydrothiophene 1,1-dioxdes is generally thought to proceed in a concerted manner,[21] it is at least conceivable that the expulsion of sulfur dioxide from **16a** and **16b** might occur via a stepwise radical (path B) or ionic (path C) pathway. For example, thermolysis of **16a,b** might result in the homolytic scission of the sulfur–carbon bond to give diradicals which would undergo cyclization to the new diradicals **22a,b**. Loss of sulfur dioxide might then lead to the diradicals **20a,b**, the vinylcyclobutanes **21a,b**, or the dienes **9a,b**. Alternatively, heterolytic cleavage, which might be induced by the electron-rich enamine or enamide function, of the sulfur–carbon bond could result in the formation of the zwitterions **23a,b** which would lose sulfur dioxide either to give the vinylcyclobutanes **21a,b** or the dienes **9a,b**.

In order to obtain evidence which would aid in the further elucidation of the mechanistic pathways involved in these unusual cycloaddition reactions, a more careful examination of the thermolysis of the enamide **16b** was undertaken in hopes of isolating stable intermediates. As mentioned previously, the thermolysis of the enamide **16b** for only 3.5 min in refluxing xylene afforded the enamido diene **9b**, albeit in low yield since considerable amounts of the starting material **16b** were also recovered. Of even greater significance is the important observation that the vinylcyclobutane **21b** is isolated in virtually quantitative yield when either the enamide **16b** is heated in refluxing benzene (30 h), toluene (1.5 h), and xylene (15 min) or the isolated enamido diene

(19) (a) Belleau, B. *J. Am. Chem. Soc.* **1953**, *75*, 5765. *Can. J. Chem.* **1956**, *35*, 651. (b) Mondon, A.; Seidel, P.-R. *Chem. Ber.* **1971**, *104*, 2937.

(20) We wish to thank Professor Raymond E. Davis (The University of Texas, Austin) for this structure determination.

(21) (a) Mock, W. L. *J. Am. Chem. Soc.* **1966**, *88*, 2857. (b) McGregor, S. D.; Lemal, D. M. *Ibid.* **1966**, *88*, 2858.

(22) It should be noted, however, that, if the enamino diene and enamido diene were formed with an internal cis double bond, either fused or bridged ring systems could be reasonably produced (see ref 2).

(23) For a discussion see: Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 5650, and references cited therein.

(24) For examples of thermal reactions of alkenes and dienes which produce vinylcyclobutanes via a stepwise cycloaddition process involving diradical intermediates, see: (a) Bartlett, P. D. *Q. Rev., Chem. Soc.* **1970**, *24*, 473. (b) Stewart, Jr., C. A. *J. Am. Chem. Soc.* **1972**, *94*, 635. (c) Bartlett, P. D.; Jacobson, B. M.; Walker, L. E. *Ibid.* **1973**, *95*, 146. (d) Bartlett, P. D.; Mallet, J. J.-B. *Ibid.* **1976**, *98*, 143. (e) Oppolzer, W.; Achini, R.; Pfenninger, E.; Weber, H. P. *Helv. Chim. Acta* **1976**, *59*, 1186.

(25) For a general discussion of the diradical mechanism for thermal pericyclic reactions, see: Firestone, R. A. *Tetrahedron* **1977**, *33*, 3009.

9b is thermolyzed in refluxing xylene (15 min). A single vinylcyclobutane **21b** appears to be formed in these cycloaddition reactions, but the configuration of the carbon bearing the vinyl group has not been established since it is not a matter of great importance. In the ^{1}H NMR spectrum of **21b**, there are three vinylic protons which appear in the characteristic pattern of a terminal vinyl group, δ 4.93–5.15 (m, 2 H) and 5.65–5.95 (m, 1 H). Additional support for the gross structure of this novel vinylcyclobutane was obtained by its conversion by catalytic hydrogenation into a dihydro derivative, **24b**. In the ^{1}H NMR spectrum of **24b**, the presence of an ethyl group is clearly evident by the appearance of a triplet (3 H, J = 7Hz) at δ 0.7 and by a distorted quartet (2 H) at δ 1.18–1.45. The subsequent reduction of the lactam **24b** with lithium aluminum hydride afforded the amine **24a** in 72% overall yield. When the vinylcyclobutane **21b** was heated in xylene at reflux (6 h), it undewent facile rearrangement to give the more stable 2-azabicyclo[3.3.1]nonene **17b**.

These data are completely consistent with the view that the unexpected bridged cycloadduct **17b** was produced from the enamido diene **9b** via the intermediate vinylcyclobutane **21b** which is probably formed by a stepwise, thermal [2 + 2] cycloaddition. Thus, initial closure of the enamido diene **9b** would afford the diradical **20b**. Since the enamido diene **9b** will exist predominantly in the s-trans conformation, the allylic moiety of the diradical **20b** will necessarily be transoid, and subsequent kinetic cyclization can produce only the vinylcyclobutane **21b**. In view of the estimated barrier to rotation of the allyl radical of $\geq$17 kcal,[26] it seems unlikely that thermal isomerization of the transoid allyl radical to the cisoid one could compete with either the collapse of the diradical **20b** to give the vinylcyclobutane **21b** or the reversion of **20b** to the starting enamido diene **9b**. The subsequent rearrangement of the vinylcyclobutane **21b** to the more stable 2-azabicyclo[3.3.1]nonene **17b** probably commences with the homolytic scission of the C(4)–C(4a) bond to give either the cisoid form of the diradical **20b** which can then cyclize to **17b** or the transoid form which would undergo closure as before to give **21b**.

Attention was then directed toward determining whether vinylcyclobutanes might also be involved in the transformation of the enamine **16a** into **17a**. Thus, treatment of the lactam **21b** with lithium aluminum hydride produced the unstable amino vinylcyclobutane **21a**, which proved to be difficult to isolate in pure form. However, upon the thermolysis of crude **21a** in refluxing xylene, rapid (<4 min) conversion to **17a** ensued. Although it could be demonstrated that the vinylcyclobutane **21a** does undergo smooth thermal rearrangement to **17a**, it has not been possible to detect the vinylcyclobutane **21a** in the reaction mixture during the thermolysis of **16a** to give **17a**. However, in view of the rapid transformation of **21a** → **17a**, speculation of **21a** as an intermediate in the conversion of **16a** → **17a** seems to be justified.

Conclusions

On the basis of the foregoing experiments, it now seems reasonable to conclude that the thermolysis of the enamide **16b** initially affords the enamido diene **9b**, which then undergoes a remarkably facile, thermal [2 + 2] cycloaddition reaction, probably via the diradical **20b**, to give the vinylcyclobutane **21b**. Upon continued thermolysis, **21b** then suffers smooth rearrangement to form the more stable, bridged [4 + 2] cycloadduct **17b**. Although the diradical pathway depicted in Scheme III (path A) appears to provide the most satisfactory explanation for the observed experimental results, the possible intermediacy of either the diradical **22b** or the zwitterion **23b** cannot yet be rigorously excluded. It has not proven feasible to elucidate all of the mechanistic details involved in the related transformation of the latent enamino diene **16a** to give the 2-azabicyclo[3.3.1]nonene **17a**, but a similar reaction pathway seems reasonable. Even though the desired spirocyclic compounds **10a** and **10b** were not produced in these reactions, the observations reported herein remain highly significant as they appear to represent the first examples of cycloaddition reactions between the electron-rich dienophiles such as enamines and enamides with unactivated butadienes. In consideration of the poor donor–acceptor properties of the dienophile and the diene in these transformations, it is remarkable indeed that the experimental conditions required to effect the cycloaddition reaction are so mild. Moreover, it is now evident that some care must be occasionally exercised in predicting the regiochemical course of intramolecular [4 + 2] cycloaddition reactions, perhaps particularly when the electronic properties of the dienophile and the diene are not complementary. Previously the formation of a bicyclo[4.3.0]nonene was routinely observed as a result of an intramolecular [4 + 2] cycloaddition of a 1,3-(*E*),8-triene.[2]

Other intramolecular [4 + 2] cycloaddition reactions of enamines and enamides are under active investigation. We have, for example, recently observed that certain endocyclic enamides do undergo intramolecular [4 + 2] cycloadditions to form fused heterocyclic ring systems such as hydrolulolidines and hydrojulolidines.[11] These and other results will be reported independently.

Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. All boiling points are uncorrected. ^{1}H NMR spectra were determined on a Varian A-60A or HA-100 spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in δ units downfield from the internal reference, tetramethylsilane (Me_4Si). Singlet, doublet, triplet, quartet, and multiplet are abbreviated as s, d, t, q, and m, respectively, and J stands for the coupling constant measured in hertz (Hz). The ^{13}C NMR spectra were determined on either a Bruker WH-90 FT or a Varian FT-80A spectrometer, and the chemical shifts are reported in δ units downfield from internal Me_4Si. The infrared spectra (IR) were recorded on a Beckman IR-5A spectrophotometer using chloroform as solvent. Low-resolution mass spectra were obtained on a Du Pont (CEC) 21-491 instrument, and the high-resolution mass spectra were obtained on a Du Pont (CEC) 21-110 instrument. GLC analyses were performed on a Varian Aerograph 2700 equipped with a thermal conductivity detector and a 5 ft × 0.25 in. 1.5% OV-101, Chromosorb HP column unless otherwise noted. Preparative high-performance liquid chromatography (LC) was performed on a Waters Prep LC 500 using two Prep PAK columns. Glassware was oven dried prior to use. The tetrahydrofuran (THF) was freshly distilled from potassium/benzophenone, and the ether was distilled from sodium. The *n*-butyllithium–hexane and the methyllithium–ether were purchased from Alfa Inorganics, Danvers, Mass., and titrated prior to use. All reactions involving organometallic reagents were conducted under an atmosphere of dry nitrogen or argon. Some microanalyses were performed by Chemalytics, Inc., Tempe, Ariz.

3,5-Hexadienoyl Chloride (7). To a solution of lithium diisopropylamide [generated from diisopropylamine (20.2 g, 0.20 mmol) in anhydrous THF (200 mL) and *n*-butyllithium (0.20 mmol, 2.45 N hexane)] at −10 °C was added dropwise a solution of sorbic acid (**11b**, 10.0 g, 0.09 mmol) in anhydrous THF (50 mL) under dry nitrogen. After the addition was complete, the reaction mixture was stirred at room temperature for another 1 h and then quenched with 3 N HCl (200 mL). The layers were separated, and the aqueous layer was extracted with ether (3 × 150 mL) and dried ($MgSO_4$). The excess solvent was evaporated under reduced pressure to give 10.0 g of 3,5-hexadienoic acid (**12b**,[14] 100%) which was dissolved in anhydrous benzene (100 mL). Thionyl chloride (21.4 g, 0.18 mol) was added dropwise, and the mixture was stirred at room temperature for 18 h. The excess thionyl chloride and solvent were removed under reduced pressure, and the product was distilled to give 9.8 g (84%) of the pure acid chloride 7 as a clear liquid: bp 79–81 °C (50 mm); IR 914, 1004, 1393, 1786 cm^{-1}; NMR δ 3.63 (d, 2 H, J = 4 Hz), 5.05–6.55 (complex, 5 H); mass spectrum m/e 130, 102, 95, 89, 67 (base), 41; exact mass 130.0184 (calcd for C_6H_7OCl, 130.0185).

Ethyl Hexa-3,5-dienoate (12a). Compound **12a** was prepared in 88% yield by the deconjugation of ethyl sorbate (**11a**) according to the method of Stevens:[15] bp 87–88 °C (30 mm); IR 1712 cm^{-1}; NMR δ 1.25 (t, 3 H, J = 7 Hz), 3.10 (d, 2 H, J = 6 Hz), 4.14 (q, 2 H, J = 7 Hz), 4.91–6.69 (complex, 5 H); ^{13}C NMR δ 14.23, 38.05, 60.66, 116.76, 125.82, 134.39, 136.53, 171.32; mass spectrum m/e 140 (base), 67; exact mass 140.0840 (calcd for $C_8H_{12}O_2$, 140.0837).

Hexa-3,5-dien-1-ol (13). A solution of ethyl hexa-3,5-dienoate (**12a**, 31.0 g, 221 mmol) in anhydrous ether (30 mL) was added dropwise to a suspension of lithium aluminum hydride (11.0 g, 290 mmol) in anhydrous ether (200 mL). After the addition was completed, the reaction

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mixture was heated at reflux for 15 h. With cooling in an ice bath, water was carefully added dropwise to destroy the excess hydride until the hydrogen evolution ceased. After 2 N H_2SO_4 (100 mL) was added to dissolve the white solid, the layers were separated, and the aqueous layer was extracted with ether (3 × 300 mL). The combined organic layers were washed with saturated $NaHCO_3$ (100 mL) and dried ($MgSO_4$). After removal of excess solvent under reduced pressure, the crude material was distilled to give 20.0 g (92%) of pure **13**: bp 79–80 °C (20 mm) [lit.[13] bp 82 °C (30 mm)]; IR 1615, 3413 cm^{-1}; NMR δ 2.32 (q, 2 H, J = 6 Hz), 3.01 (broad s, 1 H), 3.63 (t, 2 H, J = 6 Hz), 4.85–6.65 (complex, 5 H); ^{13}C NMR δ 35.96, 61.87, 115.72, 130.82, 133.53, 137.02; mass spectrum m/e 98, 68, 67 (base), 41; exact mass 98.0732 (calcd for $C_6H_{10}O$; 98.0732).

2,5-Dihydro-2-(2-hydroxyethyl)thiophene 1,1-Dioxide (14a). In a glass bomb were placed 3,5-hexadien-1-ol (**13**, 19.6 g, 200 mmol) and hydroquinone (1.0 g). The mixture was cooled to −78 °C with a dry ice bath under a drying tube, and sulfur dioxide (30 mL) was condensed. The bomb was sealed, and the solution was stirred at room temperature for 15 h. After the bomb was cooled to −78 °C and carefully opened, water (150 mL) was added, and the solution was thoroughly washed with hexane (4 × 150 mL). The aqueous layer was then saturated with NaCl and extracted with CH_2Cl_2 (3 × 200 mL), and the combined organic layers were dried ($MgSO_4$). Removal of excess solvent under reduced pressure afforded 27.5 g (85%) of crude **14a** as a thick oil for which no further purification was required. An analytical sample was obtained by preparative LC using ethyl acetate as the eluting solvent: IR 1129, 1307, 3484 cm^{-1}; NMR δ 1.53–2.51 (m, 2 H), 3.02 (br s, 1 H), 3.60–4.20 (complex, 5 H), 6.08 (s, 2 H); mass spectrum m/e 162, 98, 67 (base), 64. Anal. ($C_6H_{10}O_3S$) C, H.

2-(2,5-Dihydro-1,1-dioxothienyl)acetic Acid (15a). Sulfur dioxide (10 mL) was condensed at −78 °C into a pressure bottle containing 3,5-hexadienoic acid (**12b**, 5.23 g, 44.6 mmol) and hydroquinone (250 mg). The pressure bottle was sealed and the reaction mixture stirred at 40 °C for 48 h. The excess sulfur dioxide was then allowed to evaporate. The crude product thus obtained was washed with ether (3 × 20 mL) and recrystallized (ethyl acetate) to provide 5.57 g (71%) of pure **15a** as a white, powdery solid: mp 116–117 °C; IR 1120, 1140, 1321, 1718 cm^{-1}; NMR (Me_2SO-d_6) δ 2.68 (d, 2 H, J = 7 Hz), 3.82 (m, 2 H), 3.93–4.20 (m, 1 H), 6.10 (s, 2 H). Anal. ($C_6H_8SO_4$) C, H.

2-(2,5-Dihydro-1,1-dioxothienyl)acetyl Chloride (15b). Thionyl chloride (6.8 g, 57.0 mmol) was added slowly to a stirred solution of the acid **15a** (5.0 g, 28.0 mmol) in dry CH_2Cl_2 (25 mL). The resulting mixture was stirred at room temperature for 18 h, at which time the mixture was homogeneous. The excess thionyl chloride and solvent were evaporated under reduced pressure, and the crude product thus obtained was recrystallized from ethyl acetate–hexane (5:1) to give 4.9 g (90%) of pure **15b** as white needles: mp 49–50 °C; IR 1120, 1140, 1319, 1792 cm^{-1}; NMR δ 3.39 (dd, 2 H, J = 4, 7 Hz), 3.82 (m, 2 H), 4.02–4.32 (m, 1 H), 6.01 (m, 2 H); exact mass 193.9801 (calcd for $C_6H_7SO_3Cl$, 193.9804).

1-Methylene-3,4-dihydro-2-(2′-(2′,5′-dihydro-1′,1′-dioxothienyl))-acetylisoquinoline (16b). To a solution of 1-methyl-3,4-dihydroisoquinoline (**8**,[12] 1.45 g, 10.0 mmol) and triethylamine (1.11 g, 10.0 mmol) in dry benzene (20 mL) was added dropwise at room temperature a solution of acid chloride **15b** (2.34 g, 12.0 mmol) dissolved in dry benzene (10 mL), and the mixture was stirred at room temperature for 12 h. The triethylamine hydrochloride was removed by suction filtration, and the filtrate was concentrated under reduced pressure. The crude product thus obtained was then recrystallized from ethyl acetate–hexane (2:1) to give 2.03 g (67%) of **16b** as white needles: mp 132–133 °C dec; IR 1117, 1136, 1318, 1408, 1631 cm^{-1}; NMR δ 2.82–3.17 (complex, 4 H), 3.67 (m, 2 H), 4.00 (t, 2 H), 4.13–4.43 (m, 1 H), 5.14 (d, 1 H, J = 1 Hz), 5.78 (d, 1 H, J = 1 Hz), 6.00 (s, 2 H), 7.10–7.32 (m, 3 H), 7.50–7.75 (m, 1 H); mass spectrum m/e 303, 239, 144, 104, 95 (base). Anal. ($C_{16}H_{17}NSO_3$) C, H, N.

11-Aza-2,3,4,4a,9,10,10a-heptahydro-1-oxo-4-vinyl-3,4a-methanophenanthrene (21b). A solution of the enamide **16b** (200 mg, 0.66 mmol) in dry degassed toluene (15 mL) was heated at reflux under nitrogen for 1.5 h. The solvent was evaporated under reduced pressure, and the crude vinylcyclobutane **21b** was purified by preparative LC using ethyl acetate–hexane (4:1) as the eluting solvent. The crude product was recrystallized (hexane) to give 151 mg (95%) of pure **21b** as pale yellow prisms: mp 86–87 °C; IR 1404, 1623, 1727 cm^{-1}; ^1H NMR δ 1.89 (d, 1 H, J = 10 Hz), 2.50–2.86 (complex, 6 H), 3.31 (m, 1 H), 3.84 (t, 2 H, J = 6 Hz), 4.93–5.15 (complex, 2 H), 5.65–5.95 (complex, 1 H), 7.10–7.50 (m, 4 H); ^{13}C NMR δ 65.88, 119.07, 132.44, 168.60; mass spectrum m/e 239, 224, 144, 115, 41 (base). Anal. ($C_{16}H_{17}NO$) C, H, N.

11-Aza-2,3,4,4a,9,10,10a-heptahydro-1-oxo-3,4a-(1′-propeno)-phenanthrene (17b). Method A. The enamide **16b** (600 mg, 1.98 mmol) was dissolved in dry degassed xylene (50 mL) and heated at reflux under nitrogen for 7 h. The solvent was evaporated under reduced pressure, and the residual oil was triturated with hexane to give the cycloadduct **17b**, which was recrystallized from hexane to yield 406 mg (97%) of pure **17b** as a white, granular solid: mp 95–96.5 °C; IR 1618 cm^{-1}; NMR δ 1.78 (d, 1 H, J = 5 Hz), 2.36–3.14 (complex, 9 H), 4.78–5.03 (m, 1 H), 5.58–6.00 (m, 2 H), 7.10–7.28 (m, 4 H); mass spectrum m/e 239, 198, 184 (base), 144, 77. Anal. ($C_{16}H_{17}NO$) C, H, N.

Method B. A solution of vinylcyclobutane lactam **21b** (151 mg, 0.63 mmol) in dry degassed xylene (15 mL) was heated at reflux for 6 h under nitrogen to afford 148 mg (98%) of the lactam **17b** which was identical with that prepared by method A above.

11-Aza-2,3,4,4a,9,10,10a-heptahydro-1-oxo-4-ethyl-3,4a-methanophenanthrene (24b). The vinylcyclobutane lactam **21b** (200 mg, 0.8 mmol) in acetic acid (3 mL) was stirred with 10% Pt/C (150 mg) under hydrogen (1 atm) at room temperature for 5 h, and the catalyst was removed by suction filtration. The solution was neutralized with 4 N NaOH and extracted with ether (3 × 15 mL). The solvent was evaporated under reduced pressure to give 186 mg (93%) of the lactam **24b**: IR 1620 cm^{-1}; ^1H NMR δ 0.7 (t, 3 H, J = 7 Hz), 1.18–1.45 (m, 2 H), 1.75–1.93 (m, 1 H), 2.41–2.88 (complex, 7 H), 3.83 (t, 2 H, J = 5.5 Hz), 7.05–7.50 (complex, 4 H); ^{13}C NMR δ 11.07, 18.29, 52.53, 169.75; mass spectrum m/e 241, 226, 198 (base), 146, 115; exact mass 241.1455 (calcd for $C_{16}H_{19}NO$, 241.1467).

11-Aza-1,2,3,4,4a,9,10,10a-octahydro-4-ethyl-3,4a-methanophenanthrene (24a). A mixture of the lactam **24b** (186 mg, 0.77 mmol) and lithium aluminum hydride (150 mg, 3.8 mmol) in dry ether (15 mL) was stirred at room temperature for 4 h. The excess lithium aluminum hydride was destroyed by the sequential addition of H_2O (0.15 mL), 4 N NaOH (0.15 mL), and H_2O (0.45 mL). Removal of the precipitated solids by suction filtration and extractive workup (ether) of the filtrate gave 134 mg (77%) of amine **24a**: ^1H NMR δ 0.58 (t, 3 H, J = 7.5 Hz), 1.37 (q, 2 H, J = 7.5 Hz), 1.78–3.10 (complex, 12 H), 6.93–7.52 (m, 4 H); ^{13}C NMR δ 11.39, 17.90, 65.79; mass spectrum m/e 227, 212, 184, 145 (base). Picrate (recrystallized from ethanol): mp 124–125 °C dec. Anal. ($C_{22}H_{24}N_4O_7$) C, H, N.

11-Aza-1,2,3,4,4a,9,10,10a-octahydro-3,4a-(1′-propeno)phenanthrene (17a). Method A. A 50-mL round-bottom flask containing freshly distilled triflic anhydride[16] (2.17 g, 8.1 mmol), potassium carbonate (12 g), and CH_2Cl_2 (20 mL) was cooled to −60 °C under dry nitrogen. 2,5-Dihydro-2-(2-hydroxyethyl)thiophene 1,1-dioxide (**14a**, 1.35 g, 8.4 mmol) in CH_2Cl_2 (2 mL) was added dropwise to this mixture with vigorous stirring. After the mixture was stirred at −60 °C for 1 h and then at room temperature for another 1.5 h, 1-methyl-3,4-dihydroisoquinoline (**8**,[12] 0.74 g, 5.1 mmol) in CH_2Cl_2 (2 mL) was injected rapidly, and the resulting solution was stirred at room temperature for 16 h. The solvent was then evaporated under reduced pressure, and water (20 mL) was added. The aqueous solution was extracted with ether (3 × 20 mL), and the combined ether layers were extracted with 1 N HCl (20 mL). The aqueous layer was then washed with ether (2 × 20 mL) and made alkaline to pH 9 with 4 N NaOH. The resulting aqueous solution was extracted with ether (3 × 50 mL), and the combined extracts were dried ($MgSO_4$). Removal of the excess solvent under reduced pressure afforded a brown oil which could not be purified and fully characterized but was presumably the masked enamino diene **16a**. The crude **16a** thus obtained was dissolved in dry xylene (50 mL), and the resulting solution was then heated at reflux under dry nitrogen for 8 h. The excess solvent was removed under reduced pressure to afford the crude product **17a**. A careful column chromatography on alumina (10 g) with hexane gave 0.41 g (36%) of pure **17a**. An analytical sample was obtained by preparative GLC (5% Carbowax 20M, firebrick): ^1H NMR δ 0.95–3.36 (complex, 13 H), 5.70–5.90 (m, 2 H), 6.85–7.21 (m, 4 H); ^{13}C NMR δ 56.06, 128.96, 129.61, 134.49, 144.76; mass spectrum m/e 225 (base), 224, 210, 158; exact mass 225.1520 (calcd for $C_{16}H_{19}N$, 225.1517). The hydrobromide salt was prepared and recrystallized as white rods from acetone, mp 265–266 °C dec. Anal. ($C_{16}H_{20}BrN$) C, H, N.

Method B. A mixture of the lactam **17b** (130 mg, 0.54 mmol) and lithium aluminum hydride (100 mg) in dry ether (10 mL) was stirred at room temperature for 12 h. The excess lithium aluminum hydride was destroyed by the sequential addition of H_2O (0.1 mL), 4 N NaOH (0.1 mL), and H_2O (0.3 mL). Removal of the precipitated solids followed by an extractive workup (ether) afforded 110 mg (91%) of the amine **17a** which was identical in all respects with that obtained by method A.

Method C. The vinylcyclobutane lactam **21b** (200 mg, 0.83 mmol) was treated with lithium aluminum hydride (150 mg) in dry ether (15 mL) at room temperature for 4 h to afford 140 mg (75%) of the amino vinylcyclobutane **21a**, which without purification was dissolved in dry, degassed xylene (10 mL) and heated at reflux for 4 min under nitrogen. The crude reaction mixture was extracted with 1 N HCl (3 × 5 mL). The aqueous layer was washed with ether (2 × 5 mL), saturated with

NaCl, and made alkaline with 1 N NaOH. The basic solution was then extracted with ether (2 × 10 mL), and the combined ether extracts were dried ($MgSO_4$). The excess solvent was evaporated under reduced pressure, and the crude product was purified by preparative GLC (5% SE-30 on ABS 80/90) to give 44 mg (32%) of the amine **17a** which was identical in all respects with the samples prepared by methods A and **B**.

11-Aza-1,2,3,4,4a,9,10,10a-octahydro-3,4a-propanophenanthrene (18). To a solution of alkene **17a** (225 mg, 1 mmol) in glacial acetic acid (8 mL) was added 10% Pt/C (200 mg), and the reaction mixture was stirred under hydrogen at room temperature and atmospheric pressure for 4 h. After removal of the catalyst by filtration, the mixture was carefully made alkaline with 4 N NaOH until pH 9 and then extracted with ether (4 × 20 mL). The combined organic layers were washed with saturated brine (10 mL) and dried ($MgSO_4$). Evaporation of excess solvent under reduced pressure afforded 193 mg (85%) of pure **18**. An analytical sample was obtained by preparative GLC (5% Carbowax 20M, firebrick): ^1H NMR δ 1.00–3.50 (complex, 17 H), 7.00–7.33 (m, 4 H); ^{13}C NMR δ 55.14, 134.29, 145.28; mass spectrum *m/e* 227, 185, 184 (base), 171, 170; exact mass 227.1680 (calcd for $C_{16}H_{21}N$, 227.1674). The hydrogen bromide salt was recrystallized from 2-butanone, mp 238–239 °C dec.

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Electron-Transfer-Initiated Reactions of Organic Peroxides. Reaction of Phthaloyl Peroxide with Olefins and Other Electron Donors[1]

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Abstract: The reaction of phthaloyl peroxide with a variety of compounds capable of reacting as one- or two-electron donors was investigated. The products and the kinetics of these reactions indicate that the rate-limiting step is the transfer of one electron from the reactant to the peroxide. This conclusion was substantiated by investigating these reactions by laser flash photolysis. This study showed conclusively that odd-electron intermediates are formed in the reaction of phthaloyl peroxide with ground- and excited-state electron donors. These reactions may be prototypical of a general class of electron-transfer-initiated transformations.

To a large extent, the reactions and the relative reactivities of closed-shell organic reagents are formulated in terms of classical concepts of Lewis acidity and basicity. Thus, most transformations of such molecules are conceptualized as the result of the interaction of an electron-pair donor (nucleophile) with an electron-pair acceptor (electrophile). Indeed, this formalism serves remarkably well and has contributed greatly to our understanding of chemical reactivity. Over the years, evidence has accumulated in support of another, less widely recognized, mode of reaction for closed-shell organic reagents. In this mode, the initiating process of the reaction is the transfer of a single electron to produce odd-electron intermediates. The general sequence of events for these reactions is electron transfer followed by reaction of the odd-electron intermediates to give eventually, by coupling, disproportionation, or a second electron transfer, even-electron products. This sequence has been found to predominate in a group of chain reactions generally described by the $S_{RN}1$ mechanism.[3,4]

The reactions of organic peroxides with reagents capable of serving as one- or as two-electron donors have served as a focus for much of the debate over the role played by electron transfer. The reaction of benzoyl peroxide (BPO) with amines is a typical case. Horner's early investigation of the reaction of BPO with dimethylaniline led him to postulate a reaction sequence initiated by one-electron transfer from the amine to the peroxide.[5] This proposal neatly explained the rapid formation of radical-derived products and was shown later to be consistent with the effect of substituents on the reaction kinetics for symmetrically substituted benzoyl peroxides[6] and substituted amines.[7] Horner's postulate

Scheme I

Path A (Electron Transfer):

$$ArN(Me)_2 + (PhCO_2)_2 \xrightarrow{\text{electron transfer}} \left[ArN(Me)_2^{+\cdot}\ PhCO_2^{\cdot}\ PhCO_2^{-}\right] \quad (1)$$

$$\left[ArN(Me)_2^{+\cdot}\ PhCO_2^{\cdot}\ PhCO_2^{-}\right] \xrightarrow{\text{cage escape}} \text{Free radicals} \qquad \xrightarrow{\text{in cage reaction}} \text{Non-radical products} \quad (2)$$

Path B (Nucleophilic Attack):

$$ArN(Me)_2 + (PhCO_2)_2 \longrightarrow Ar\overset{+}{N}(Me)_2O_2CPh + PhCO_2^{-} \quad (3)$$

$$Ar\overset{+}{N}(Me)_2O_2CPh \xrightarrow{\text{homolysis}} Ar\overset{+}{N}(Me)_2 + PhCO_2 \qquad \xrightarrow{\text{elimination}} \left[ArN(Me)=CH_2\right]^{+} + PhCO_2H \quad (4)$$

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