Intramolecular Munchnone Cycloadditions: Preparation and Chemistry of the Intramolecular Dipolar Cycloadducts

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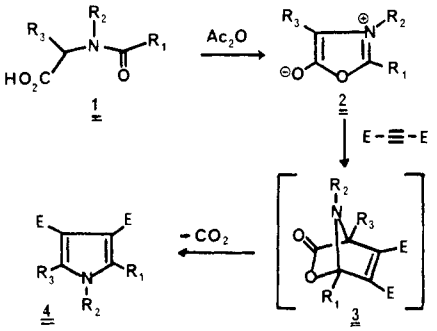
A series of munchnone derivatives containing an internal π-bond were generated in situ by treating several *N*-(*o*-allylphenyl) and *N*-(*o*-vinylbenzyl) amino acids with acetic anhydride. The oxazoloquinolinone and oxazoloisoquinolinone cycloadducts formed corresponded to an intramolecular 1,3-dipolar cycloaddition of the mesoionic species across an unactivated olefinic π-bond with retention of the elements of carbon dioxide. The regioselectivity of the internal cycloaddition was explored and found to be markedly dependent on the substituent groups present. The chemical behavior of these novel bicyclic compounds with organometallic reagents was investigated and found to produce tricyclic lactols and multifunctionalized benzazepines.

Mesoionic compounds have been known for many years and have been extensively utilized as substrates in 1,3-dipolar cycloadditions.[1-3] Of the known mesoionic heterocycles, munchnones have generated considerable interest in recent years.[4-8] These compounds can be considered as unstable mesoionic Δ^2-oxazolium 5-oxides of type **2** with azomethine ylide structure.[1] Munchnones are readily prepared by cyclodehydration of *N*-acyl amino acids **1** with reagents such as acetic anhydride.[1-3] The reaction of munchnones with acetylenic dipolarophiles constitutes a pyrrole synthesis of broad scope.[9-16] 1,3-Dipolar cycloaddition of acetylenes to the Δ^2-oxazolium 5-oxide **2**, followed by cycloreversion of carbon dioxide from the initially formed adduct **3**, gives pyrrole derivatives **4** in good yield.



Cycloaddition studies of munchnones with other dipolarophiles have resulted in practical, unique syntheses of numerous functionalized monocyclic and ring annulated heterocycles.[1-3] The development of effective approaches to bridged heterocyclic ring systems is an important topic in organic synthesis.[17] Intramolecular 1,3-dipolar cycloaddition offers a potent methodology for the formation of these compounds.[18] As part of a research program designed to uncover new cycloadditions of mesoionic heterocycles, we initiated a study dealing with the chemistry of munchnones containing a π-bond in close proximity to the dipole center. An attractive feature associated with the internal cycloaddition of mesoionic compounds is the opportunity to control the stereochemistry of the products at several centers. In systems where the dipole and dipolarophile are linked by several atoms, the highly ordered transition state will also induce useful regiochemical control. In an earlier paper we reported on the intramolecular cycloaddition of munchnones derived from *N*-(*o*-allylphenyl)alanines and *N*-(*o*-allylphenyl)-2-phenylglycines.[19] Subsequent studies showed that the regioselectivity of the internal cycloaddition was markedly dependent on the substituent groups present. In this paper we report our recent findings dealing with the effect of substituents and geometry on the cycloaddition reaction. The chemistry of the resulting internal cycloadducts with several organometallic reagents is also described.

Results and Discussion

The intramolecular 1,3-dipolar cycloaddition reactions of the alanine-derived 2-unsubstituted and 2-trifluoromethyl-substituted munchnones **7a** and **7b** were initially examined. Treatment of *N*-(*o*-allylphenyl)alanine (**5**) in 88% formic acid with acetic anhydride provided *N*-formyl-*N*-(*o*-allylphenyl)alanine (**12a**). It is of interest to note that these *N*-formylation conditions[20] did not effect

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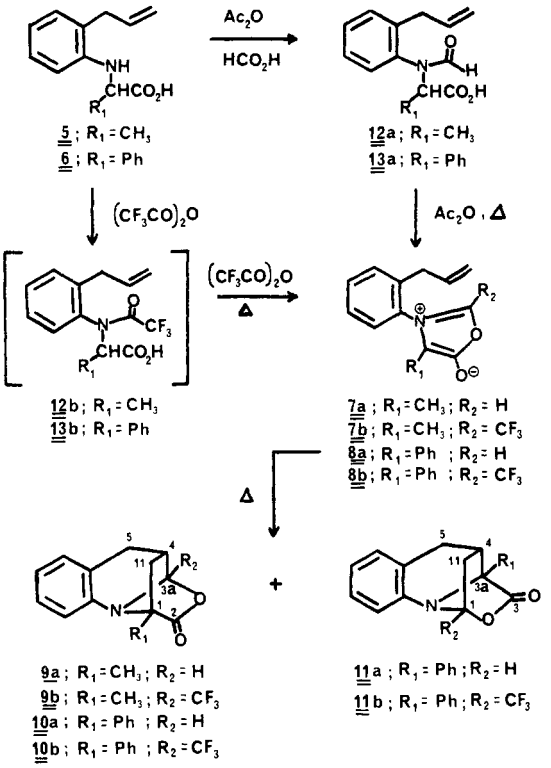
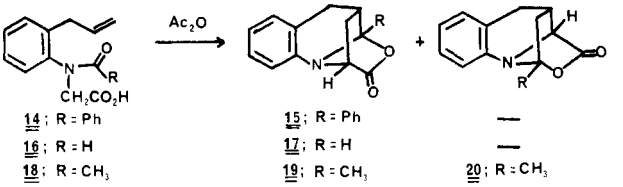
cyclodehydration to **7a** or cycloaddition. However, reaction of **12a** with acetic anhydride at 55 °C afforded regiospecifically cycloadduct **9a** in 75% yield. Similarly, treatment of **5** with 2.5 equiv of trifluoroacetic anhydride in toluene at 55 °C gave, via the intermediacy of **12b** and munchnone **7b**, a 70% yield of cycloadduct **9b** as the exclusive regioisomer. In neither case were there any signs of another regioisomer in the crude reaction mixture. Thus, alanine-derived munchnones of type **7** afford only cycloadducts of type **9** regardless of the nature of the 2-substituent (R_2).



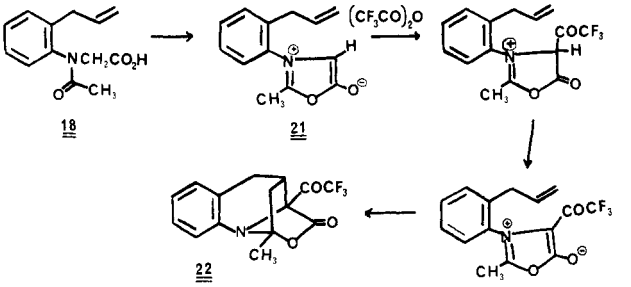
The intramolecular cycloaddition reactions of the 2-phenylglycine derived 2-unsubstituted and 2-trifluoromethyl substituted munchnones **8a** and **8b** were also studied. Heating a sample of *N*-formyl-*N*-(*o*-allylphenyl)-2-phenylglycine (**13a**) with acetic anhydride at 55 °C afforded a mixture of oxazolo[3,2-*a*]quinolin-2(1*H*)-one **10a** (26%) and oxazolo[3,4-*a*]quinolin-3(3a*H*)-one **11a** (58%). Similarly, addition of 2.5 equiv of trifluoroacetic anhydride to a suspension of **6** followed by heating at 55 °C yielded, via **13b** and **8b**, a mixture of cycloadducts **10b** (4%) and **11b** (78%). No attempt was made to isolate the intermediate munchnone since Huisgen has previously shown the Δ^2-oxazolium 5-oxide system to be extremely reactive.[4-8] The azomethine ylide functionality of the mesoionic species undergoes an intramolecular 1,3-dipolar cycloaddition with the unactivated π-bond to give the observed products.

The structural assignment of cycloadducts **9**–**11** is based on their spectral data (see Experimental Section). In the ^{1}H NMR spectra of **9a** and **10a**, the signals for proton H_{3a} appear at δ 5.23 and 5.38, respectively, with no coupling to proton H_4. However, the signal for H_1 in **11a** appears as a doublet at δ 5.64 (J = 2.5 Hz) which is coupled to H_{11} (δ 1.84 ppm; J = 13.5, 2.5, and 2.0 Hz) but not to $H_{11'}$. Examination of molecular models reveals that the dihedral angle between H_{3a} and H_4 (for **9a** and **10a**) and between H_1 and $H_{11'}$ (for **11a**) is close to 90 °C thereby accounting for the absence of coupling. Additionally, the aromatic region of the ^{1}H NMR spectra of 1-phenyl substituted oxazoloquinolinones **10** shows the presence of an appreciably shielded doublet which is absent in the spectra of the 3a-phenyl substituted oxazoloquinolinones **11**. Pertinent chemical shifts and coupling constants for the intramolecular cycloadducts are given in the Experimental Section.

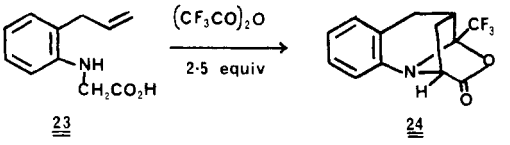
We also studied the cycloaddition chemistry of *N*-benzoyl-*N*-(*o*-allylphenyl)glycine (**14**). Treatment of **14** with acetic anhydride produced a single cycloadduct (**15**) in 77% yield. The NMR spectrum of **15** exhibits a diagnostic doublet for H_1 at δ 4.20 ($J_{1,11}$ = 5.3 Hz). Heating a sample of the closely related *N*-formyl-*N*-(*o*-allylphenyl)glycine (**16**) with acetic anhydride at 100 °C for 18 h yields a single regioisomer in 80% which was assigned as **17** on the basis of its spectral data. In contrast to the above systems, treatment of *N*-acetyl-*N*-(*o*-allylphenyl)-glycine (**18**) with acetic anhydride at 100 °C produced an 85:15 mixture of cycloadducts **19** and **20** in 92% overall yield.



It is of interest to note that the cyclodehydration–cycloaddition reactions of **18** with trifluoroacetic anhydride followed a different course both chemically and regiochemically. The exclusive product obtained was assigned as oxazoloquinolinone **22**. In this case, acylation of the



munchnone intermediate **21** occurs at a faster rate than internal cycloaddition. There are several cases in the literature where trifluoroacetic anhydride has been incorporated into the mesoionic species.[21-23] It should be pointed out that trifluoroacetic anhydride can still be employed as a cyclodehydrating reagent without subsequent acylation of the 4-unsubstituted munchnone if a large excess of anhydride is avoided. Thus, addition of 2.5 equiv of trifluoroacetic anhydride to a suspension of *N*-(*o*-allylphenyl)glycine (**23**) at 0 °C followed by heating at 100 °C for 8.5 h afforded cycloadduct **24** as the exclusive product.



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The above results clearly indicate that the nature of the substituent groups present on the munchnone ring play an important role in controlling the regioselectivity of cycloaddition. When the 4-position of the munchnone ring is unsubstituted or substituted with a methyl group, the C-2 substituent has little effect on the orientation of the cycloaddition. However, when the 4-position is substituted with a phenyl group, the C-2 substituent has profound influence on the regiochemistry of cycloaddition.

In view of the stringent requirements associated with the intramolecular cycloaddition of 1,3-dipoles,[18] we throught it worthwhile to consider what effect a variation in the spatial proximity between the dipole and dipolarophile would have on the course of the intramolecular dipolar cycloaddition reaction. This led us to study the cycloaddition behavior of the munchnone derived from *N*-acyl-*N*-(*o*-vinylphenyl) amino acids **25**. Unfortunately, all attempts to detect intramolecular cycloaddition from this system failed. Presumably, the azomethine ylide portion of the munchnone **26** and the internal dipolarophile cannot attain the required "parallel-plane" approach and intramolecular 1,3-dipolar cycloaddition does not occur. The situation is different with the homologous *N*-(*o*-vinylbenzyl)munchnone system **28**. With this system, the transition state for cycloaddition can be arranged in such a way as to allow the p orbitals of the alkene to lie in a plane parallel to the plane of the 1,3-dipole. Thus, reaction of *N*-acetyl-*N*-(*o*-vinylbenzyl)glycine (**27a**) with acetic anhydride produced a mixture of four products which could be readily separated by high pressure liquid chromatography. The major products were assigned as oxazolo[3,2-*b*]isoquinolin-2(3*H*)-one **29a** (38%) and oxazolo[3,4-*b*]isoquinolin-1(5*H*)-one **30a** (25%) on the basis of their spectral data. The H_3 proton of cycloadduct **29a** appears as a doublet at δ 3.83 (J = 6.0 Hz) and is coupled to H_{11} (δ 1.85; J = 14.0, 6.0, and 2.0 Hz) but not to $H_{11'}$. In contrast, proton H_{10a} of cycloadduct **30a** appears as a singlet at δ 3.43 and is not coupled to H_{10}. Examination of molecular models reveals that H_3 and $H_{11'}$ (for **29a**) and H_{10a} and H_{10} (for **30a**) have dihedral angles close to 90°. Additionally, two minor cycloadducts (**29b** and **30b**) were also isolated which correspond to the incorporation of an acetyl group into the bicyclic framework. When the thermolysis of **27a** was carried out with *N*,*N*′-dicyclohexylcarbodiimide (DCC) in benzene, the acetylated cycloadducts **29b** and **30b** were not formed. Interestingly, treatment of **27a** with an excess of trifluoroacetic anhydride afforded a single regioisomer (**30c**) in 75% yield.

We also studied the cycloaddition behavior of the closely related *N*-benzoyl-*N*-(*o*-vinylbenzyl)glycine system (**27d**). In this case an 87% yield of a 3:2 mixture of regioisomeric cycloadducts (**29d** and **30d**) was obtained when **27d** was treated with acetic anhydride. It should be noted that treatment of **27d** with an excess of trifluoroacetic anhydride produced a single trifluoroacetylated cycloadduct in 82% which was assigned as oxazolo[3,4-*b*]isoquinolin-1-(5*H*)-one **30e**. The fact that the trifluoroacetylated cycloadducts **30c** and **30e** were formed in high yield attests to the increased reactivity of the trifluoroacetylated munchnone system. It would appear that the rate of internal cycloaddition of the munchnone **28** is slower than the rate of trifluoroacetylation. This is not the case with the acetyl system since only small quantities of the acetylated regioisomers (i.e., **29b** and **30b**) were formed. Most interestingly, the regioselectivity with the trifluoroacetylated system is opposite that normally encountered.

The cycloaddition behavior of a series of *N*-acyl-*N*-(*o*-vinylbenzyl)alanines **31** was also explored. Heating a sample of *N*-acetylalanine (**31a**) with acetic anhydride gave rise to a mixture of two regioisomers which were assigned as cycloadducts **32a** (34%) and **33a** (51%). Similarly, the reaction of *N*-benzoylalanine (**31b**) with acetic anhydride gave cycloadducts **32b** and **33b** (2:4.5) in 72% yield. It should be noted that the regioselectivity in this series differs somewhat from that observed with the *N*-(*o*-vinylbenzyl)glycine series.

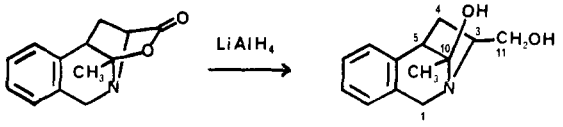
The structural assignments of these cycloadducts were made on the basis of their spectral data. A particularly useful correlation for structural purposes involves ^{13}C NMR chemical shifts of the C_{10} and C_{11} carbons. For the oxazolo[3,2-*b*]isoquinolin-2(3*H*)-ones **29** and **32**, the ^{13}C NMR chemical shift for the C_{10} carbon atom always appears at a lower field than the chemical shift for the C_{11} carbon. The opposite correlation exists for the isomeric oxazolo[3,4-*b*]isoquinolin-1(5*H*)-ones **30** and **33**. Additionally, the ^1H NMR chemical shift for the H_5 AB quartet of cycloadducts **29** and **32** uniformly appears downfield relative to the H_5 AB quartet for the corresponding regioisomeric cycloadducts **30** and **33**.

The results obtained with the intramolecular cycloaddition reactions of the *N*-(*o*-vinylbenzyl)-substituted munchnones indicates that the regioselectivity of this system is more heavily influenced by the substituent at the C-4 position than by the substituent at the C-2 position. These reactions are also unique in that the products obtained correspond to 1:1-cycloadducts which have retained the elements of carbon dioxide. This represents one of the few examples of an isolable primary cycloadduct of a munchnone and an olefin. The fact that the intramolecular cycloadducts do not lose carbon dioxide easily is undoubtedly due to Bredt rule considerations. The nitrogen lone pair of electrons in the rigid tricyclic system is not correctly aligned to participate in the extrusion of CO_2 to give an azomethine ylide.

The 1,3-dipolar cycloaddition of mesoionic systems is generally thought to be a LUMO(dipole)–HOMO(dipolarophile) controlled process.[24,25] There have been some

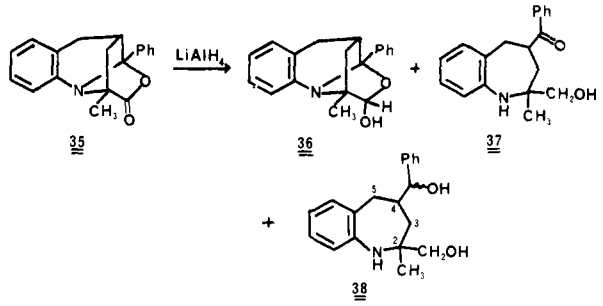
reports, however, which suggest that a HOMO(dipole)–LUMO(dipolarophile) controlled reaction may be more appropriate.[16] MINDO calculations have shown that the C-4 position of munchnones contains the largest coefficient in the HOMO while the C-2 position contains the largest coefficient in the LUMO.[26] The effect of a substituent on dipole energies is expected to be a function of the magnitude of the coefficient at the site of attachment. Thus, for the dipole HOMO's, substituent effects should be in the order "anionic" terminus > "neutral" terminus > central atom, for position of substituent attachment. For the LUMO, the corresponding order is expected to be "neutral" terminus ~ central atom > "anionic" terminus. We can assume that the C_4 carbon of a munchnone has more "anionic" character due to stabilization of the negative charge by the adjacent carbonyl group. Based on these assumptions, we would expect that C-4 substituents will have a greater effect on the HOMO of the dipole. Thus, a HOMO-controlled process would be most consistent with the observed substituent effects. The energy difference between the dipole (HOMO)–dipolarophile (LUMO) and dipole (LUMO)–dipolarophile (HOMO) of the *N*-(*o*-vinylbenzyl)munchnones may be sufficiently small as to allow substituents a greater degree of regiochemical control. It should be noted, however, that the regiochemistry of the *N*-(*o*-allylphenyl)munchnone cycloadditions cannot be easily accommodated by Frontier MO theory. Mesoionic compounds having high local charge densities give rise to a complex inhomogeneous field in the vicinity of the approaching dipolarophile and van der Waal's energy considerations may be quite important in providing some insight into the regiochemistry of these cycloadditions.[27] Frontier MO theory alone does not easily account for the distribution of products obtained from the above systems. It seems reasonable to assume that steric factors also play a role in determining the regiochemical outcome of the above cycloadditions.

The oxazoloquinoline and oxazolisoquinoline ring systems obtained from the above cycloaddition studies represent novel heterocyclic compounds which potentially can be used as synthetic precursors for the Amaryllidaceae class of alkaloids. Accordingly, we decided to examine the chemistry of these tricyclic ring systems so as to evaluate their potential use in alkaloid synthesis. Reaction of oxazoloquinolinone **29a** with lithium aluminum hydride gave a white crystalline solid whose structure was assigned as methano-2*H*-benzazepine-3-methanol **34** on the basis of its spectral data. Proton-decoupling experiments showed that irradiation of the signal at δ 3.22 (H_3) caused the signals for H_4, $H_{4'}$, H_{11}, and $H_{11'}$ to collapse. Irradiation of the doublet at 3.08 ppm (J = 5.3 Hz) for H_5 caused proton H_4 to collapse to a doublet of doublets. This observation indicates a dihedral angle of close to 90° for protons $H_{4'}$ and H_5.



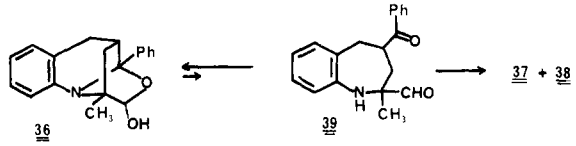
29a 34

The LAH-induced reduction of the closely related oxazolo[3,2-*a*]quinolin-2(*H*)-one system **35**[19] was also investigated. Treatment of **35** with 1 equiv of LAH at 25 °C



35 36 37 38

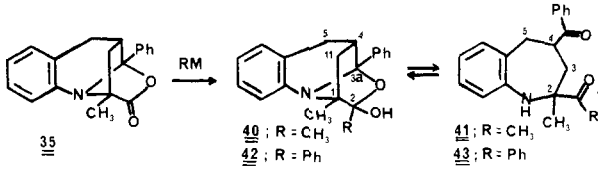
for 5 h gave rise to a mixture of three products which could be readily separated by silica gel chromatography. The first compound to be eluted from the column was identified as 3a,4-dihydro-1-methyl-3a-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-ol (**36**) (6%) on the basis of its spectral properties. The IR spectrum reveals the absence of a carbonyl group and the presence of an OH stretch at 3530 cm^{-1}. The mass spectrum shows a molecular ion at 293 which is consistent with a molecular formula of $C_{19}H_{19}NO_2$. The NMR spectrum of **36** is quite similar to **35**, which indicates that the tricyclic oxazolo[3,2-*a*]quinoline structure is still intact and that the lactone has been reduced to a lactol. An interesting feature of the ^1H NMR spectrum of **36** is the presence of a weak singlet at δ 9.55. This signal is probably due to the aldehyde proton of **39** which is in tautomeric equilibrium with **36**.



36 39

The major product (48%) isolated from the column was identified as ketone **37** on the basis of its spectral data. A strong band at 1680 cm^{-1} in the IR clearly indicates the presence of a benzoyl group. The NMR spectrum of **37** reveals a pattern substantially different from the spectrum of **36**. A lessening of the rigidity in this molecule is also evidenced by a decrease in the relative proton chemical shift difference of the H_3 protons (ΔH_3 = 0.12 ppm) vs. **5** (ΔH_{11} = 0.63 ppm). The third product (mixture of diastereomers) corresponded to structure **38** which is derived from the further reduction of **37**. This was demonstrated by an independent reduction of both **36** and **37** to give **38**. Oxazoloquinolinol **36** could be oxidized back to the starting lactone **35** by Sarett's reagent. The formation of benzoyl benzazepine **37** is presumed to be derived from the reduction of tautomer **39**.

We also found that the oxazolo[3,2-*a*]quinolinone system reacts quite readily with organometallic reagents. Thus, the addition of methyllithium to **35** gave a 95% yield of a mixture of oxazolo[3,2-*a*]quinolinol **40** and its tautomer **41** in a 2:3 ratio. All attempts to separate this mixture were



35 40 ; R = CH3 42 ; R = Ph 41 ; R = CH3 43 ; R = Ph

unsuccessful. It is assumed that both compounds exist in tautomeric equilibrium in solution. The NMR spectrum of the mixture shows a singlet at δ 1.48 corresponding to the methyl group attached to the lactol moiety as well as a singlet at δ 2.28 corresponding to the acetyl group of tautomer **41**. Additionally, the ^{13}C NMR spectrum of the

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mixture shows three singlets at δ 78.6, 97.4, and 104.1 corresponding to the C-1, C-3a, and C-2 carbon atoms of compound **40** while the three singlets at δ 63.6, 201.9, and 209.3 correspond to the C-2 carbon atom and the carbonyl carbons of the acetyl and benzoyl groups of tautomer **41**. In a related fashion, treatment of **35** with phenylmagnesium bromide afforded mostly lactol **42** together with very small quantities of the ring opened tautomer **43**. The above results illustrate that the addition of organometallic reagents to the oxazoloquinolinone ring system provides access to tricyclic lactols which, in turn, can undergo ring opening to give multifunctionalized benzazepine derivatives.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 283 or 735B infrared spectrometer. ^{1}H NMR spectra were obtained on a Varian EM-390, FT-80A, Nicolet FT-360, and a XL-100 spectrometer. ^{13}C NMR spectra were recorded on a Varian FT-80A spectrometer operating at 20 MHz. Microanalysis were performed at FMC Corporation, Princeton, NJ, and by Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV.

Treatment of *N*-Formyl-*N*-(*o*-allylphenyl)alanine (12a) with Acetic Anhydride. A solution contain 1.28 g of *N*-formyl-*N*-(*o*-allylphenyl)alanine (**12a**) in 11 mL of acetic anhydride was heated with stirring at 55 °C for 3 h. The solution was cooled, and 55 mL of water was added to the reaction mixture. After being stirred for 30 min, the aqueous reaction mixture was extracted with methylene chloride. The methylene chloride extracts were washed with water, a saturated aqueous sodium bicarbonate solution, and water. The methylene chloride layer was dried over magnesium sulfate and concentrated under reduced pressure to give a colorless solid (1.09 g). This solid was recrystallized from acetone–hexane to afford 3a,4-dihydro-1-methyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (**9a**) as a colorless crystalline solid (0.88 g, 75%): mp 86–87 °C; IR (film) 1800, 1480, 1325, 1210, 1080, 1035, and 760 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.21 (dd, 1 H, J = 13.5, 2.0 Hz), 1.31 (s, 3 H), 1.84 (dd, 1 H, J = 13.5, 7.5 Hz), 2.78 (dd, 1 H, J = 18.0, 2.5 Hz), 2.75–2.99 (m, 1 H), 3.22 (dd, 1 H, J = 18.0, 4.0 Hz), 5.23 (s, 1 H), 6.84–7.43 (m, 4 H); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 12.4, 32.5, 34.5, 37.0, 72.1, 92.5, 126.8–140.9 (6 lines), 174.7. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.24; H, 5.80; N, 6.35.

Thermolysis of *N*-(*o*-Allylphenyl)alanine (5) with Trifluoroacetic Anhydride. To a stirred suspension of 1.43 g of *N*-(*o*-allylphenyl)alanine (**5**)[19] in 15 mL of toluene at 0 °C was added 3.67 g of trifluoroacetic anhydride. After the addition was complete, the reaction mixture was diluted with 15 mL of ether and washed with water, a saturated aqueous sodium bicarbonate solution, and water. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give a brown solid. This material was chromatographed over silica gel using a 20% acetone–hexane mixture as the eluent to give a solid which was recrystallized from acetone–hexane to afford 3a,4-dihydro-1-methyl-3a-(trifluoromethyl)-1,4-methano-5*H*-oxazolo[3,2-*a*]-quinolin-2(1*H*)-one (**9b**) as a colorless crystalline solid (1.39 g, 70%): mp 93–94 °C; IR (film) 1820, 1330, 1210, 1130, 1065, 1025 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.26 (s, 3 H), 1.27 (dd, 1 H, J = 16 Hz), 2.97–3.17 (m, 1 H), 3.80 (br d, 1 H, J = 16 Hz), 6.97–7.37 (m, 4 H); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 12.4, 33.9 (q, 1.6 Hz), 35.7, 37.6, 73.0, 94.5 (q, J = 33.6 Hz), 121.9 (q, 281.5 Hz), 127.3–139.7 (6 lines), 171.4. Anal. Calcd for $C_{14}H_{12}F_3NO_2$: C, 59.37; H, 4.27; N, 4.94. Found: C, 59.16; H, 4.09; N, 4.95.

Thermolysis of *N*-Formyl-*N*-(*o*-allylphenyl)-2-phenylglycine (13a) in Acetic Anhydride. A solution containing 2.07 g of *N*-formyl-*N*-(*o*-allylphenyl)-2-phenylglycine (**13a**) in 14 mL of acetic anhydride was heated with stirring at 55 °C for 3 h. Workup, as for **9a**, gave a light yellow oil, which was shown by NMR spectroscopy to be a mixture of two regioisomeric cycloadducts in a 3:2 ratio. Fractional crystallization of this oil from toluene–petroleum ether afforded the regioisomeric cycloadducts. 4,5-Dihydro-3a-phenyl-1,4-methano-1*H*-oxazolo[3,4-*a*]-quinolin-3(3a*H*)-one (**11a**) (1.13 g, 58%): mp 121–122 °C; IR (film) 1790, 1150, 1100, 960, 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.84 (ddd, 1 H, J = 13.5, 2.5, 2.0 Hz), 2.31 (dd, 1 H, J = 13.5, 7.0 Hz), 2.33 (s, 1 H), 2.57–3.01 (m, 2 H), 5.64 (d, 1 H, J = 2.5 Hz), 6.82–7.54 (m, 9 H); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 31.8, 36.6, 72.4, 96.3, 125.3–141.0 (12 lines), 173.3. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.97; H, 5.38; N, 4.90.

The minor component was assigned as 3a,4-dihydro-1-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (**10a**) (0.51 g, 26%): mp 143–144 °C; IR (film) 1790, 1230, 1040, 975, 750, 695 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.94 (dd, 1 H, J = 13.5, 2.5 Hz), 2.28 (dd, 1 H, J = 13.5, 7.0 Hz), 2.88 (dd, 1 H, J = 16.0, 2.0 Hz), 2.92–3.26 (m, 1 H), 3.31 (dd, 1 H, J = 16.0, 3.0 Hz), 5.38 (s, 1 H), 6.60 (d, 1 H, J = 7.0 Hz), 6.77–7.23 (m, 3 H), 7.40 (s, 5 H); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 29.2, 34.7, 37.0, 79.3, 92.8, 126.5–141.0 (9 lines), 173.9. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.13; H, 5.30; N, 4.88.

Thermolysis of *N*-(*o*-Allylphenyl)-2-phenylglycine (6) with Trifluoroacetic Anhydride. To a stirred suspension of 2.14 g of *N*-(*o*-allylphenyl)-2-phenylglycine (**6**)[19] in 15 mL of toluene at 0 °C was added 4.20 g of trifluoroacetic anhydride. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 1 h and at 55 °C for 3 h. Workup, as for **9b**, gave a light yellow viscous oil which solidified upon standing. Examination of this material by NMR spectroscopy indicated the presence of predominantly the 3-oxo isomer **11b** with ca. 5–10% of the 2-oxo isomer **10b**. Fractional crystallization of this solid from toluene–petroleum ether afforded the regioisomeric cycloadducts. 4,5-Dihydro-3a-phenyl-1-(trifluoromethyl)-1,4-methanol-1*H*-oxazolo[3,4-*a*]quinolin-3(3a*H*)-one (**11b**) (2.16 g, 78%): mp 153–154 °C; IR (film) 1810, 1180, 1100, 975, 760, 695 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.15 (dd, 1 H, J = 13.5, 2.0 Hz), 2.60 (dd, 1 H, J = 13.5, 7.0 Hz), 2.75–2.90 (m, 2 H), 3.00–3.30 (m, 1 H), 6.85–7.53 (m, 9 H); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 32.1, 33.8, 36.2, 74.1, 100.3 (q, J = 34.1 Hz), 121.2 (q, J = 279.8 Hz), 237.3–139.3 (9 lines), 170.1. Anal. Calcd for $C_{19}H_{14}F_3NO_2$: C, 66.09; H, 4.09; N, 4.06. Found: C, 66.42; H, 4.11; N, 3.94.

The minor component was assigned as 3a,4-dihydro-1-phenyl-3a-(trifluoromethyl)-1,4-methano-5*H*-oxazolo[3,2-*a*]-quinolin-2(1*H*)-one (**10b**) (0.12 g, 4%): mp 175–176 °C; IR (film) 1810, 1450, 1225, 1195, 1115, 1065, 770, 695 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.11 (dd, 1 H, J = 13.5, 2.5 Hz), 2.43 (dd, 1 H, J = 13.5, 7.5 Hz), 2.94 (br d, 1 H, J = 17 Hz), 3.17–3.40 (m, 1 H), 3.39 (br d, 1 H, J = 17 Hz), 6.57 (d, 1 H, J = 7.5 Hz), 6.77–7.22 (m, 3 H), 7.38 (s, 5 H). Anal. Calcd for $C_9H_{14}F_3NO_2$: C, 66.09; H, 4.09; N, 4.06. Found: C, 66.33; H, 3.98; N, 3.95.

Thermolysis of *N*-Benzoyl-*N*-(*o*-allylphenyl)glycine (14) in Acetic Anhydride. A solution containing 0.33 g of *N*-benzoyl-*N*-(*o*-allylphenyl)glycine (**14**) in 10 mL of acetic anhydride was heated at 50 °C for 12 h. Workup, as for **9a**, afforded a solid which recrystallized from chloroform and hexane to give 0.28 g (77%) of a white crystalline solid, mp 143–144 °C, whose structure was assigned as 3a,4-dihydro-3a-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (**15**) on the basis of its spectral data: IR ($CHCl_3$) 3360, 1800, 1460, 1140, 1025, and 905 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.88 (ddd, 1 H, J = 13.4, 5.3, and 2.2 Hz), 2.16 (dd, 1 H, J = 13.4 and 7.4 Hz), 2.75 (dd, 1 H, J = 16.0 and 2.7 Hz), 2.84 (dd, 1 H, J = 16.0 and 3.3 Hz), 3.28 (m, 1 H), 4.20 (d, 1 H, J = 5.3 Hz), 6.95–7.55 (m, 9 H); UV (95% ethanol) 224 nm (ε 5000), 258 nm (ε 700), 262 nm (ε 790), 268 nm (ε 760), 274 nm (ε 570); m/e 277 (M^+), 249, 201, 144, and 115; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 29.8 (t), 34.9 (t), 37.2 (d), 69.2 (d), 102.1 (s), 126.6 (d), 126.8 (d), 127.4 (d), 128.1 (d), 128.5 (d), 129.2 (s), 129.5 (d), 129.6 (d), 132.2 (s), 143.1 (s), 172.4 (s). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.85; H, 5.48; N, 5.03.

Thermolysis of *N*-Formyl-*N*-(*o*-allylphenyl)glycine (16) in Acetic Anhydride. A solution of 4.38 g of *N*-formyl-*N*-(*o*-allylphenyl)glycine (**16**) in 40 mL of acetic anhydride was heated with stirring at 100 °C for 18 h. Workup, as for **9a**, gave a solid residue which was recrystallized from acetone–hexane to give 3.23 g (80%) of a colorless crystalline solid, whose structure was assigned as 3a,4-dihydro-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (**17**) on the basis of its spectral data: mp 105–106 °C; IR (neat) 1810, 1485, 1085, 1030, 975, and 765 cm^{-1}; NMR ($CDCl_3$,

100 MHz) δ 1.58 (ddd, 1 H, J = 13.0, 5.0, and 2.5 Hz), 1.87 (dd, 1 H, J = 13.0 and 6.5 Hz), 2.87 (dd, 1 H, J = 17.5 and 3.0 Hz), 2.75–2.94 (m, 1 H), 3.21 (dd, 1 H, J = 17.5 and 4.0 Hz), 4.05 (d, 1 H, J = 5.0 Hz), 5.21 (s, 1 H), 7.19 (s, 4 H); m/e 201 (M^+), 172, 158, 144, 130, 117, 91, and 77; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 26.4 (t), 34.5 (t), 35.0 (d), 67.4 (d), 93.3 (d), 126.0 (d), 126.4 (d), 126.7 (d), 128.4 (s), 128.8 (d), 141.5 (s), 172.3 (s); UV (95% ethanol) 266 nm (ε 410), 274 nm (ε 350). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.90; H, 5.57; N, 7.00.

Thermolysis of *N*-Acetyl-*N*-(*o*-allylphenyl)glycine (18) in Acetic Anhydride. A solution containing 0.53 g of *N*-acetyl-*N*-(*o*-allylphenyl)glycine (**18**) in 5 mL of acetic anhydride was heated at 100 °C for 17 h. Workup, as for **9a**, yielded a brown oil which was subjected to silica gel flash chromatography using a 10% acetone–hexane mixture as the eluent. The major fraction contained 0.45 g (92%) of a white solid which consisted of a [85:15] mixture of regioisomers. The regioisomers could be separated by fractional recrystallization from chloroform and hexane. The major isomer was assigned as 3a,4-dihydro-3a-methyl-1,4-methano-5*H*-oxazolo[3,4-*a*]quinolin-3(3a*H*)-one (**19**) on the basis of its spectral data: mp 87–88 °C; IR (KBr) 2992, 1795, 1605, 1485, 1400, 1310, 1240, 1160, 1110, 1025, 940, and 690 cm^{-1}; NMR ($CDCl_3$, 360 MHz), 1.56 (s, 3 H), 1.66 (ddd, 1 H, J = 13.5, 5.2, and 2.0 Hz), 1.98 (dd, 1 H, J = 13.5 and 7.3 Hz), 2.66 (m, 1 H), 2.80 (dd, 1 H, J = 17.0 and 2.4 Hz), 3.12 (dd, 1 H, J = 17.0 and 3.5 Hz), 4.00 (d, 1 H, J = 5.2 Hz), 7.10–7.27 (m, 4 H); UV (95% ethanol) 225 nm (sh, ε 4200), 265 (ε 470), 274 (ε 390); MS, m/e 215 (M^+), 187, 144 (base) and 130; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.8 (q), 29.6 (t), 34.7 (t), 37.8 (d), 69.0 (d), 100.2 (s), 126.8 (d), 127.4 (d), 128.6 (s), 129.4 (d), 142.6 (s), 172.8 (s). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.51; H, 6.14; N, 6.47.

The minor regioisomer was assigned the structure of 4,5-dihydro-1-methyl-1,4-methano-1*H*-oxazolo[3,4-*a*]quinolin-3-(3a*H*)-one (**20**) on the basis of its spectral properties: mp 116–117 °C; IR (KBr) 2940, 1795, 1455, 1325, 1245, 1150, 1095, 1030 and 730 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.45 (dd, 1 H, J = 13.0 and 0.90 Hz), 1.62 (s, 3 H), 2.16 (dd, 1 H, J = 13.0 and 7.3 (Hz), 2.74–2.80 (m, 2 H), 3.19 (dd, 1 H, J = 17.3 and 4.0 Hz), 3.74 (s, 1 H), 7.12–7.22 (m, 4 H); UV (95% ethanol) 230 nm (ε 3300), 265 nm (ε 400), 275 nm (ε 280); MS, m/e 215 (M^+), 187, 144, 130, and 115; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 16.6 (q), 32.0 (d), 34.4 (t), 39.0 (t), 65.4 (d), 106.9 (s), 127.0 (d), 127.9 (d), 129.2 (s), 130.2 (d), 141.2 (s), 172.7 (s).

Thermolysis of *N*-Acetyl-*N*-(*o*-allylphenyl)glycine (18) with Trifluoroacetic Anhydride. A solution containing 0.20 g of *N*-acetyl-*N*-(*o*-allylphenyl)glycine (**18**) and 1 mL of trifluoroacetic anhydride in 2 mL of benzene was stirred at 55 °C for 12 h. Workup, as for **9a**, yielded a yellow oil. This material was subjected to silica gel flash chromatography to give 0.08 g (33%) of a clear oil whose structure was assigned as 4,5-dihydro-1-methyl-3a-(trifluoroacetyl)-1,4-methano-1*H*-oxazolo-[3,2-*a*]quinolin-2(1a*H*)-one (**22**) on the basis of its spectral properties: IR ($CHCl_3$) 1800, 1760, 1610, 1580, 1455, 1345, and 830 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.54 (dd, 1 H, J = 14.0 and 2.0 Hz), 1.67 (s, 3 H), 2.32 (dd, 1 H, J = 14.0 and 7.0 Hz), 2.70 (dd, 1 H, J = 19.0 and 4.0 Hz), 3.15 (m, 1 H), 3.23 (dd, 1 H, J = 19.0 and 3.0 Hz), 7.00–7.35 (m, 4 H); MS, m/e 311 (M^+), 226, 200, 156, 128, and 115; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 16.6 (q), 32.0 (t), 34.3 (d), 40.8 (t), 77.0 (s), 107.3 (s), 115.0 (q), 127.6 (d), 127.9 (d), 128.4 (d), 130.3 (d), 139.5 (s), 167.4 (s). Anal. Calcd for $C_{15}H_{12}F_3NO_3$: C, 57.88; H, 3.86; N, 4.50. Found: C, 58.85; H, 4.32; N, 4.43.

Thermolysis of *N*-(*o*-Allylphenyl)glycine (23) with Trifluoroacetic Anhydride. To a stirred suspension of 0.96 g of *N*-(*o*-allylphenyl)glycine (**23**) in 10 mL of toluene at 0 °C was added 2.63 g of trifluoroacetic anhydride. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 1 h, at 55 °C for 1 h, and at 100 °C for 8.5 h. Workup, as for **9b**, afforded a yellow oil. This material was charomatographed over silica gel using a 10% acetone–hexane mixture as the eluent to give a colorless solid (1.00 g), which was recrystallized from acetone–hexane to afford 3a,4-dihydro-3a-(trifluoromethyl)-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (**24**) as a colorless crystalline solid (0.72 g, 53%): mp 135–136 °C; IR (film) 1830, 1210, 1195, 1135, 1100, and 765 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.79 (ddd, 1 H, J = 13.5, 5.1, 2.3 Hz), 2.13 (dd, 1 H, J = 13.5, 7.1 Hz), 2.86 (br d, 1 H, J = 17 Hz), 3.03–3.19 (m, 1 H), 3.31 (br d, 1 H, J = 17 Hz), 4.12 (d, 1 H, J = 5.1 Hz), 7.08–7.34 (m, 4 H). Anal. Calcd for $C_{13}H_{10}F_3NO_2$: C, 58.00; H, 3.74; N, 5.20. Found: C, 57.72; H, 3.65; N, 4.98.

Thermolysis of *N*-Acetyl-*N*-(*o*-vinylbenzyl)glycine (27a) with Acetic Anhydride. A mixture containing 120 mg of *N*-acetyl-*N*-(*o*-vinylbenzyl)glycine (**27a**) and 2.0 mL of acetic anhydride in 10 mL of toluene was stirred at 100 °C for 8 h. At the end of this time the solvent was removed under reduced pressure to leave behind a dark yellow oil. This material was passed through a short silica gel column using a 10% acetone–hexane mixture as the eluent to give 90 mg of a clear oil which was subjected to high pressure liquid chromatography using a 30 cm × 8 mm zorbax-cyano column with a 90:9:1 mixture of hexane:chloroform:isopropyl alcohol as the eluent. The first fraction which was obtained in less than 5% yield was assigned as 10a-acetyl-10,10a-dihydro-3-methyl-3,10-methano-3*H*-oxazolo[3,4-*b*]isoquinolin-1(5*H*)-one (**30b**) on the basis of its spectral properties: mp 127–128 °C; IR ($CHCl_3$) 1800, 1725, 1460, 1280, 910, and 880 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.74 (s, 3 H), 1.74 (dd, 1 H, J = 14.0 and 2.0 Hz), 2.20 (s, 3 H), 2.65 (dd, 1 H, J = 14.0 and 7.0 Hz), 3.60 (dd, 1 H, J = 7.0 and 2.0 Hz), 3.94 (d, 1 H, J = 18.0 Hz), 4.52 (d, 1 H, J = 18.0 Hz), 7.0–7.3 (m, 4 H); UV (95% ethanol) 273 nm (ε 2500); MS, m/e 257 (M^+), 214, 186, and 117 (base).

The second fraction contained a mixture of two isomers. These two materials were subjected to high pressure liquid chromatography using a Waters Prep 500 unit equipped with a silica gel column using a 25% ethyl acetate–hexane mixture as the eluent. The first fraction contained 30 mg (25%) of a sticky paste whose structure was assigned as 10,10a-dihydro-3-methyl-3,10-methano-3*H*-oxazolo[3,4-*b*]isoquinolin-1(5*H*)-one (**30a**) on the basis of its spectral data: IR ($CHCl_3$) 1800, 1490, 1320, 1240, 1130, 1030, and 895 cm^{-1}; NMR (CCl_4, 90 MHz) δ 1.50 (dd, 1 H, J = 14.0 and 1.5 Hz), 1.70 (s, 3 H), 2.44 (dd, 1 H, J = 14.0 and 7.0 Hz), 3.27 (dd, 1 H, J = 7.0 and 1.5 Hz), 3.43 (s, 1 H), 3.84 (d, 1 H, J = 19.0 Hz), 4.28 (d, 1 H, J = 19.0 Hz), 7.1–7.15 (m, 4 H); UV (95% ethanol) 257 nm (300), 265 nm (ε 320), 272 nm (ε 270); MS, m/e 215 (M^+), 187 (base), 144, 129, and 115; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.8 (q), 38.6 (d), 46.0 (t), 46.6 (t), 64.8 (d), 104.1 (s), 125.9 (d), 126.4 (d), 127.3 (d), 130.6 (s), 141.5 (s), 172.6 (s). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.56; H, 6.04; N, 6.51. Found: C, 72.64; H, 6.06; N, 6.47.

The second component contained 45 mg (38%) of a white crystalline solid whose structure was assigned as 10,10a-dihydro-10a-methyl-3,10-methano-5*H*-oxazolo[3,2-*b*]isoquinolin-2-(3*H*)-one (**29a**) on the basis of its spectral properties: mp 139–140 °C; IR (KBr) 1815, 1725, 1490, 1440, 1095, 990, 720, and 680 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.44 (s, 3 H), 1.85 (ddd, 1 H, J = 14.0, 6.0, and 2.0 Hz), 2.38 (dd, 1 H, J = 14.0 and 7.0 Hz), 3.30 (dd, 1 H, J = 7.0 and 2.0 Hz), 3.83 (d, 1 H, J = 6.0 Hz), 4.02 (d, 1 H, J = 18.0 Hz), 4.50 (d, 1 H, J = 18.0 Hz), 7.0–7.2 (m, 4 H); UV (95% ethanol) 262 nm (ε 2900); m/e 215 (M^+), 180, 144, 129 (base); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 15.3 (q), 37.1 (t), 44.9 (d), 49.9 (t), 64.9 (d), 100.6 (s), 125.8 (d), 126.3 (d), 126.9 (d), 131.7 (s), 141.2 (s), 172.8 (s). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.56; H, 6.04; N, 6.51. Found: C, 72.49; H, 6.06; N, 6.51.

The final fraction contained a clear oil whose structure was assigned as 3-acetyl-10,10a-dihydro-10a-methyl-3,10-methano-5*H*-oxazolo[3,2-*b*]isoquinolin-2(3*H*)-one (**29b**) on the basis of its spectral data: NMR (CCl_4, 90 MHz) δ 1.44 (s, 3 H), 2.07 (dd, 1 H, J = 14.0 and 2.0 Hz), 2.37 (dd, 1 H, J = 14.0 and 7.0 Hz), 2.41 (s, 3 H), 3.30 (dd, 1 H, J = 7.0 and 2.0 Hz), 3.95 (d, 1 H, J = 19.0 Hz), 4.37 (d, 1 H, J = 19.0 Hz), 6.9–7.2 (m, 4 H); IR ($CDCl_3$) 1795, 1720, 1520, 1400, 1370, 1220, 1160, 1110, and 935 cm^{-1}.

Treatment of *N*-Acetyl-*N*-(*o*-vinylbenzyl)glycine (27a) with Trifluoroacetic Anhydride. A solution containing 560 mg of *N*-acetyl-*N*-(*o*-vinylbenzyl)glycine (**27a**) and 3.0 g of trifluoroacetic anhydride was stirred at room temperature for 3.5 h. The excess trifluoroacetic anhydride was removed under reduced pressure, and the resulting residue was passed through a short silica gel column using a 10% acetone–hexane solution as the eluent to give 560 mg (75%) of 10,10a-dihydro-3-methyl-10a-(trifluoroacetyl)-3,10-methano-3*H*-oxazolo[3,4-*b*]isoquinolin-1(5*H*)-one (**30c**) as a white crystalline solid whose

structure was assigned on the basis of its spectral properties: mp 101–102 °C; IR (KBr) 1800, 1760, 1495, 1440, 1390, 1320, 1260, 1160, 1000, and 870 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.81 (dd, 1 H, J = 14.0 and 2.0 Hz), 1.86 (s, 3 H), 2.68 (dd, 1 H, J = 14.0 and 7.0 Hz), 3.83 (dd, 1 H, J = 7.2 Hz), 3.98 (d, 1 H, 18.0 Hz), 4.48 (d, 1 H, J = 18.0 Hz), 7.0–7.3 (m, 4 H); MS, m/e 311 (M^+), 241, 214, 199, 144, 155 (base); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 15.7 (q), 41.3 (d), 46.0 (t), 47.0 (t), 77.8 (s), 104.0 (s), 114.7 (q), 126.7 (d), 127.2 (d), 128.2 (d), 129.5 (s), 138.0 (s), 167.4 (s), 183.9 (q). Anal. Calcd for $C_{15}H_{12}F_3NO_3$: C, 57.88; H, 3.86; N, 4.50. Found: C, 57.67; H, 3.91; N, 4.41.

Thermolysis of *N*-Benzoyl-*N*-(*o*-vinylbenzyl)glycine (27d) with Acetic Anhydride. A stirred solution containing 0.16 g of *N*-benzoyl-*N*-(*o*-vinylbenzyl)glycine (**27d**) and 2 mL of acetic anhydride in 2 mL of benzene was heated at 55 °C for 5 h. Workup, as for **9a**, yielded 0.13 g (87%) of a crystalline solid which contained a mixture of two isomeric cycloadducts in a 3:2 ratio. The major isomer could be obtained as a crystalline solid, mp 206–207 °C, by fractional crystallization from a mixture of chloroform and hexane. The structure of this isomer was assigned as 10,10a-dihydro-10a-phenyl-3,10-methano-5*H*-oxazolo[3,2-*b*]-isoquinolin-2(3*H*)-one (**29d**) on the basis of its spectral data: IR ($CHCl_3$) 1800, 1460, 1130, 1100, 1000, and 930 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.05 (ddd, 1 H, J = 14.0, 5.0, and 2.0 Hz), 2.56 (dd, 1 H, J = 14.0 and 7.0 Hz), 4.01 (dd, 1 H, J = 7.0 and 2.0 Hz), 4.04 (d, 1 H, J = 18.0 Hz), 4.098 (d, 1 H, J = 5.0 Hz), 4.44 (d, 1 H, J = 18.0 Hz), 6.75–7.65 (m, 9 H); UV (95% ethanol) 263 nm (ϵ 770), 274 nm (ϵ 640); MS, m/e 277 (M^+), 249, 219, 160, 146, and 117; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 37.5 (t), 43.4 (d), 50.6 (t), 65.4 (d), 102.4 (s), 125.9 (d), 126.1 (d), 126.6 (d), 126.8 (d), 128.4 (d), 129.0 (d), 129.6 (d), 131.8 (s), 132.1 (s), 141.6 (s) and 172.5 (s). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.54; N, 5.05. Found: C, 77.71; H, 5.48; N, 4.97.

The minor isomer was assigned the structure of 10,10a-dihydro-3-phenyl-3,10-methano-3*H*-oxazolo[3,4-*b*]isoquinolin-1-(5*H*)-one (**30d**) on the basis of its spectral data: mp 191–192 °C; IR (neat) 1795, 1495, 1360, 1330, 1220, 1070, 905, and 710 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.17 (dd, 1 H, J = 14.0 and 1.5 Hz), 2.90 (dd, 1 H, J = 14.0 and 7.0 Hz), 3.48 (dd, 1 H, J = 7.0 and 1.5 Hz), 3.65 (d, 1 H, J = 19.0 Hz), 3.72 (s, 1 H), 4.17 (d, 1 H, J = 19.0 Hz), 6.80–7.75 (m, 9 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 38.1 (d), 43.1 (t), 46.7 (t), 65.0 (d), 106.3 (s), 125.9 (d), 126.4 (d), 126.5 (d), 127.4 (d), 128.8 (d), 129.0 (d), 130.5 (d), 131.0 (s), 131.8 (s), 141.4 (s), 172.3 (s); UV (95% ethanol) 247 nm (ϵ 1370), 256 nm (ϵ 1240), 263 (ϵ 1030), 268 (ϵ 690). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.82; H, 5.49; N, 5.02.

Treatment of *N*-Benzoyl-*N*-(*o*-vinylbenzyl)glycine (27d) with Trifluoroacetic Anhydride. A solution containing 0.15 g of *N*-benzoyl-*N*-(*o*-vinylbenzoyl)glycine (**27d**) and 2.0 mL of trifluoroacetic anhydride was stirred at room temperature for 3 h. Workup, as for **9a**, gave 0.16 g (82%) of a white crystalline solid, mp 105–106 °C, whose structure was assigned as 10,10a-dihydro-3-phenyl-10a-(trifluoroacetyl)-3,10-methano-3*H*-oxazolo[3,4-*b*]isoquinolin-1(5*H*)-one (**30e**) on the basis of its spectral data: IR (KBr) 2930, 1755, 1455, 1280, 1085, 1070, 1000, and 770 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.39 (dd, 1 H, J = 14.0 and 2.0 Hz), 3.10 (dd, 1 H, J = 14.0 and 7.0 Hz), 3.73 (d, 1 H, J = 18.0 Hz), 4.00 (dd, 1 H, J = 5.0 and 2.0 Hz), 4.33 (d, 1 H, J = 18 Hz), 6.85–7.80 (m, 9 H); MS, m/e 373 (M^+), 276, 262, 232, 172, 129, 117 (base); ^{13}C NMR ($CDCl_3$, 50 MHz), 40.8 (d), 44.2 (t), 46.4 (t), 78.0 (s), 105.8 (s), 114.8 (q, CF_3), 126.7 (d), 127.1 (d), 128.2 (d), 128.4 (d), 129.0 (d), 129.1 (d), 129.8 (s), 130.4 (s), 131.2 (d), 138.1 (s), 167.1 (s), and 183.8 (s); UV (95% ethanol) 256 nm (ϵ 1200), 263 (ϵ 1200), 269 nm (ϵ 1060). Anal. Calcd for $C_{20}H_{14}F_3NO_3$: C, 64.34; H, 3.78; N, 3.75. Found: C, 64.26; H, 3.79; N, 3.73.

Thermolysis of *N*-Acetyl-*N*-(*o*-vinylbenzyl)alanine (31a) in Acetic Anhydride. A solution containing 30.2 mg of *N*-acetyl-*N*-(*o*-vinylbenzyl)alanine (**31a**) in 2 mL of acetic anhydride was stirred at 55 °C for 6 h. Workup, as for **9a**, afforded a brown residue. This material was subjected to silica gel flash chromatography using a 10% acetone–hexane mixture as the eluent to give 238 mg (85%) of a colorless oil. This material was subjected to high pressure liquid chromatography using a silica gel column and eluting with a mixture of hexane–chloroform–isopropyl alcohol (96:1:3) to give two isomers in a 3:2 ratio. The first fraction contained the minor isomer whose structure was assigned as 10,10a-dihydro-3,10a-dimethyl-3,10-methano-5*H*-oxazolo[3,2-*b*]-isoquinolin-2(3*H*)-one (**32a**) on the basis of its spectral properties: IR ($CHCl_3$) 1800, 1590, 1460, 1395, 1310, 1205, 1160, 1125, 1060, and 900 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.40 (s, 3 H), 1.46 (s, 3 H), 1.50 (dd, 1 H, J = 14.0 and 2.0 Hz), 2.30 (dd, 1 H, J = 14.0 and 7.0 Hz), 3.29 (dd, 1 H, J = 7.0 and 2.0 Hz), 4.05 (d, 1 H, J = 19.0 Hz), 4.42 (d, 1 H, J = 19.0 Hz), 6.90–7.30 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 12.3 (s), 15.5 (s), 43.8 (t), 47.3 (t), 47.6 (d), 68.6 (s), 99.9 (s), 126.0 (d), 126.5 (d), 126.6 (d), 127.2 (d), 131.6 (s), 141.6 (s), 175.5 (s); MS, m/e 229 (M^+), 201, 144, and 115; UV (95% ethanol) 214 nm (ϵ 10100).

The major isomer was assigned the structure of 10,10a-dihydro-3,10a-dimethyl-3,10-methano-3*H*-oxazolo[3,4-*b*]isoquinolin-1(5*H*)-one (**33a**) on the basis of its spectral data: IR ($CHCl_3$) 2950, 1590, 1460, 1390, 1330, 1275, 1170, 1125, 1080, 990, and 860 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.10 (s, 3 H), 1.60 (dd, 1 H, J = 14.0 and 2.0 Hz), 1.63 (s, 3 H), 2.48 (dd, 1 H, J = 14.0 and 7.0 Hz), 2.94 (dd, 1 H, J = 7.0 and 2.0 Hz), 3.88 (d, 1 H, J = 19.0 Hz), 4.17 (d, 1 H, J = 19.0 Hz), 6.85–7.20 (m, 4 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 11.9 (s), 16.1 (s), 42.2 (t), 45.1 (d), 48.6 (t), 67.3 (s), 102.4 (s), 126.2 (d), 126.5 (d), 126.8 (d), 127.2 (d), 130.4 (s), 140.4 (s), 175.5 (s).

Thermolysis of *N*-Benzoyl-*N*-(*o*-vinylbenzyl)alanine (31b) with Acetic Anhydride. A stirred solution containing 0.38 g of *N*-benzoyl-*N*-(*o*-vinylbenzyl)alanine (**31b**) in 5 mL of acetic anhydride was heated at 55 °C for 3 h. Workup, as for **9a**, yielded a solid material. This material was subjected to silica gel flash chromatography using a 10% acetone–hexane mixture as the eluent. The first fraction contained 0.18 g (50%) of an oil whose structure was assigned as 10,10a-dihydro-10a-methyl-3-phenyl-3,10-methano-3*H*-oxazolo[3,4-*b*]isoquinolin-1(5*H*)-one (**33b**) on the basis of its spectral data: IR ($CHCl_3$) 1790, 1495, 1440, 1340, 1205, 1155, 1065, 985, and 835 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.27 (s, 3 H), 2.31 (dd, 1 H, J = 13.2 and 1.4 Hz), 2.96 (dd, 1 H, J = 13.2 and 7.0 Hz), 3.18 (dd, 1 H, J = 7.0 and 1.4 Hz), 3.76 (d, 1 H, J = 19.0 Hz), 4.09 (d, 1 H, J = 19.0 Hz), 6.86–7.66 (m, 9 H); MS, m/e 291 (M^+), 264, 149, and 117; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 12.1 (q), 41.6 (d), 45.3 (t), 45.6 (t), 67.6 (s), 104.5 (s), 126.3 (d), 126.4 (d), 126.8 (d), 127.2 (d), 128.7 (d), 128.8 (d), 130.3 (d), 130.7 (s), 132.3 (s), 140.4 (s), 175.2 (s).

The second fraction contained 0.06 g (17%) of a white crystalline solid whose structure was assigned as 10,10a-dihydro-3-methyl-10a-phenyl-3,10-methano-5*H*-oxazolo[3,2-*b*]isoquinolin-2(3*H*)-one (**32b**) on the basis of its spectral data: mp 211–212 °C; IR ($CHCl_3$) 1795, 1590, 1360, 1260, 1155, 1110, 1065, 1000, 925, and 850 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.62 (s, 3 H), 1.74 (dd, 1 H, J = 13.3 and 1.7 Hz), 2.51 (dd, 1 H, J = 13.3 and 7.2 Hz), 4.00 (dd, 1 H, J = 7.2 and 1.7 Hz), 4.09 (d, 1 H, J = 18.6 Hz), 4.28 (d, 1 H, J = 18.6 Hz), 6.86–7.66 (m, 9 H); MS, m/e 291 (M^+), 263, 201, 149, and 117; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 12.6 (q), 43.8 (t), 45.4 (d), 47.6 (t), 68.7 (s), 101.5 (s), 125.9 (d), 126.2 (d), 126.6 (d), 126.8 (d), 128.4 (d), 129.0 (d), 129.6 (d), 132.0 (s), 132.2 (s), 141.7 (s), 175.0 (s). Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.27; H, 5.92; N, 4.77.

Reduction of 10,10a-Dihydro-10a-methyl-3,10-methano-5*H*-oxazolo[3,2-*b*]isoquinolin-2(3*H*)-one (29a) with Lithium Aluminum Hydride. To a solution containing 0.10 g of 10,10a-dihydro-10a-methyl-3,10-methano-5*H*-oxazolo[3,2-*b*]isoquinolin-2(3*H*)-one (**29a**) in 10 mL of anhydrous ether was added 0.02 g of lithium aluminum hydride. After stirring at 0 °C for 7 h, a few drops of water were added to hydrolyze the remaining hydride. The mixture was filtered, and the filtrate was concentrated under reduced pressure to leave behind a yellow solid which was recrystallized from chloroform and hexane to give a white crystalline solid (55%), mp 131–132 °C, whose structure was assigned as 1,3,4,5-tetrahydro-10-hydroxy-10-methyl-2,5-methano-2*H*-benzazepine-3-methanol (**34**) on the basis of its spectral data: IR (KBr) 1490, 1390, 1260, 1190, 1110, 1065, 970, 790, and 740 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.46 (s, 3 H), 1.98 (dd, 1 H, J = 12.1 and 8.4 Hz), 2.34 (m, 1 H), 3.08 (d, 1 H, J = 5.3 Hz), 3.22 (m, 1 H), 3.52 (dd, 1 H, J = 11.5 and 4.6 Hz), 3.93 (d, 1 H, J = 17.0 Hz), 4.02 (dd, 1 H, J = 11.5 and 3.3 Hz), 4.39 (d, 1 H, J = 17.0 Hz), 5.93 (bs, 2 H), 6.9–7.3 (m, 4 H); UV (95% ethanol) 264 nm (ϵ 330), 272 nm (ϵ 280); MS, m/e 219 (M^+), 188, 160, 151, 129, and 117; ^{13}C NMR ($CDCl_3$, 50 MHz) or 22.7 (q), 36.3 (t), 50.3 (d), 58.8 (t), 65.0 (t), 66.8 (d), 77.2 (s), 126.4 (d), 127.0

(d), 127.1 (d), 128.0 (d), 132.8 (s), 142.0 (s). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82; N, 6.39. Found: C, 70.93; H, 7.87; H, 6.31.

Treatment of 3a,4-Dihydro-1-methyl-3a-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (35) with Lithium Aluminum Hydride. To a stirred solution containing 1.10 g of 3a,4-dihydro-1-methyl-3a-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (**35**) in 30 mL of anhydrous ether at room temperature was added 0.14 g of lithium aluminum hydride. After stirring at room temperature for 5 h, a few drops of water were added to hydrolyze the remaining hydride. The solution was filtered, and the filtrate was concentrated under reduced pressure to give 0.95 g of a white solid. This material was subjected to silica gel flash chromatography using a 10% acetone–hexane mixture as the eluent. The first fraction contained 0.07 g (6%) of a white solid whose structure was assigned as 3a,4-dihydro-1-methyl-3a-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-ol (**36**) on the basis of its spectral properties: mp 127–128 °C; IR ($CHCl_3$ 1485, 1420, 1350, 1250, 1125, 1045, 830, and 710 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.20 (s, 3 H), 1.22 (dd, 1 H, J = 13.0 and 2.0 Hz), 1.86 (dd, 1 H, J = 13.0 and 7.0 Hz), 2.63 (m, 2 H), 3.03 (m, 1 H), 3.18 (d, 1 H, J = 13.0 Hz), 4.85 (d, 1 H, J = 13.0 Hz), 6.8–7.5 (m, 9 H); UV (95% ethanol) 232 nm (ϵ 3970); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.3 (q), 35.5 (t), 37.2 (t), 41.0 (d), 75.4 (s), 97.8 (s), 100.55 (d), 126.0 (d), 127.6 (d), 128.0 (d), 128.3 (d), 128.5 (d), 129.6 (d), 130.4 (s), 135.8 (s), 142.8 (s); MS, m/e 293 (M^+), 264, 188, 158, and 105 (base). Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.63; H, 6.55; N, 4.76.

The second fraction contained 0.53 g (48%) of a white solid whose structure was assigned as phenyl 2,3,4,5-tetrahydro-2-(hydroxymethyl)-2-methyl-1*H*-1-benzazepin-4-yl ketone (**37**) on the basis of its spectral data: mp 42–43 °C; IR ($CHCl_3$) 1680, 1580, 1450, 1330, 1260, 1185, 1105, 1030, 930, 890, and 680 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 0.99 (s, 3 H), 1.64 (dd, 1 H, J = 13.5 and 2.0 Hz), 1.76 (dd, 1 H, J = 13.5 and 13.0 Hz), 2.86 (m, 2 H), 3.0 (bs, 2 H), 3.45 (d, 1 H, J = 10.0 Hz), 3.50 (d, 1 H, J = 10 Hz), 3.55 (m, 1 H), 6.71 (d, 1 H, J = 3.5 Hz), 6.82 (t, 1 H, J = 7.0 Hz), 7.00 (m, 24), 7.40 (t, 2 H, J = 7.0 Hz), 7.49 (m, 1 H), 7.88 (d, 2 H, J = 7.0 Hz); UV (95% ethanol) 241 nm (ϵ 19 100), 281 nm (ϵ 2900); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.8 (q), 37.8 (t), 40.6 (d), 41.1 (t), 55.4 (s), 71.9 (t), 121.8 (d), 121.9 (d), 127.4 (d), 128.4 (d), 128.8 (d), 130.2 (d), 132.0 (s), 133.0 (d), 136.0 (s), 146.1 (s), 202.8 (s); MS, m/e 295 (M^+), 264, 174, 144, 130, and 105. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.54. Found: C, 77.13; H, 7.38; N, 4.54.

The third fraction contained 0.05 g (4%) of a white solid whose structure was assigned as a diastereomeric mixture of 2,3,4,5-tetrahydro-2-(hydroxymethyl)-4-(hydroxybenzyl)-1*H*-1-benzazepine (**38**) on the basis of its spectral data: mp 60–61 °C; IR (KBr) 1600, 1465, 1380, 1250, 1090, 750, and 680 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ isomer A δ 0.86 (s, 3 H), 1.19 (d, 1 H, J = 12.5 Hz), 1.26 (br s, 1 H), 1.34 (dd, 1 H, J = 12.5 and 12.0 Hz), 2.06 (m, 1 H), 2.2–2.8 (bs, 2 H), 2.58 (dd, 1 H, J = 13.6 and 10.0 Hz), 3.08 (d, 1 H, J = 13.6 Hz), 3.38–3.47 (m, 2 H), 4.54 (d, 1 H, J = 7.0 Hz), 6.65–7.40 (m, 9 H); isomer B δ 0.93 (s, 3 H), 1.26 (bs, 1 H), 1.51 (dd, 1 H, J = 12.0 and 12.0 Hz), 1.74 (d, 1 H, J = 12.0 Hz), 2.2–2.8 (bs, 2 H), 2.49 (dd, 1 H, J = 13.6 and 10.0 Hz), 2.63 (d, 1 H, J = 13.6 Hz), 3.38–3.47 (m, 2 H), 4.48 (d, 1 H, J = 7.0 Hz), 6.65–7.40 (m, 9 H); UV (95% ethanol) 236 nm (ϵ 7220); MS, m/e 297 (M^+), 266 (base), 248, 160, 144, and 106; ^{13}C NMR ($CDCl_3$, 50 MHz) δ isomer A δ 21.6 (q), 37.6 (t), 39.4 (t), 39.6 (d), 55.6 (s), 72.4 (t), 78.9 (d), 121.3 (d), 121.6 (d), 126.8 (d), 127.8 (d), 128.5 (d), 130.3 (d), 132.4 (s), 143.3 (s), 146.2 (s); isomer B δ 21.2 (q), 36.4 (t), 39.1 (d), 40.8 (t), 55.8 (s), 72.4 (t), 78.6 (d), 121.2 (d), 121.6 (d), 126.7 (d), 126.9 (d), 127.8 (d), 128.5 (d), 130.5 (d), 132.3 (s), 143.2 (s), 146.2 (s). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71. Found: C, 75.66; H, 7.93; N, 4.47.

Treatment of 3a,4-Dihydro-1-methyl-3a-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (35) with Methyllithium. To a stirred solution containing 100 mg of 3a,4-dihydro-1-methyl-3a-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (**35**)[19] in 5 mL of anhydrous tetrahydrofuran at 0 °C was added 0.3 mL of a 1.5 M solution of methyllithium in ether. The solution was stirred for 5 h while being allowed to warm at room temperature. At the end of this time, the mixture was poured into 50 mL of ice cold water and extracted with ether. The ether extracts were washed with water and dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 120 mg of a yellow oil. This oil was subjected to silica gel flash chromatography using a 10% ethyl acetate–hexane mixture was the eluent to give 100 mg (95%) of a colorless oil which was shown to be an inseparable mixture of 3a,4-dihydro-1,2-dimethyl-3a-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]-quinolin-2(1*H*)-ol (**40**) and phenyl 2,3,4,5-tetrahydro-2-acetyl-2-methyl-1*H*-benzazepin-4-yl ketone (**41**) on the basis of their spectral properties: IR (neat) 1710, 1680, 1465, 1345, 1230, 1180, 1100, 1005, 920, and 840 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ (**40**) δ 1.16 (dd, 1 H, J = 13.3 and 2.0 Hz), 1.20 (s, 3 H), 1.48 (s, 3 H), 2.19 (dd, 1 H, J = 13.3 and 7.5 Hz), 2.56 (dd, 1 H, J = 16.9 and 2.5 Hz), 2.70 (dd, 1 H, J = 16.9 and 3.4 Hz), 3.02 (m, 1 H), 4.08 (bs, 1 H), 7.12–7.60 (m, 9 H); (**41**) δ 1.20 (s, 3 H), 2.15 (dd, 1 H, J = 13.1 and 11.9 Hz), 2.27 (dd, 1 H, J = 13.1 and 2.2 Hz), 2.28 (s, 3 H), 2.90 (dd, 1 H, J = 14.3 and 4.5 Hz), 2.97 (dd, 1 H, J = 14.3 and 3.3 Hz), 3.72 (m, 1 H), 4.77 (bs, 1 H), 6.80–8.00 (m, 9 H); UV (95% ethanol) 238 nm (ϵ 9300); MS, m/e 307 (M^+), 264, 202, 158, 105 (base); ^{13}C NMR ($CDCl_3$ 50 MHz) δ (**40**) δ 14.0 (q), 18.6 (q), 35.2 (t), 35.6 (t), 40.8 (d), 78.6 (s), 97.4 (s), 104.1 (s), 126.1 (d), 126.4 (d), 127.5 (d), 128.0 (d), 128.31 (d), 128.34 (d), 129.6 (d), 130.4 (s), 135.8 (s), 143.0 (s); (**41**) δ 22.4 (q), 24.2 (q), 37.2 (t), 39.4 (t), 40.1 (d), 63.6 (s), 122.1 (d), 127.6 (d), 128.4 (d), 128.9 (d), 130.0 (d), 131.9 (s), 133.2 (d), 135.8 (s), 145.4 (s), 201.9 (s), 209.3 (s). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.07; H, 6.96; N, 4.52.

Treatment of 3a,4-Dihydro-1-methyl-3a-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (35) with Phenylmagnesium Bromide. To a stirred solution containing 70 mg of 3a,4-dihydro-1-methyl-3a-phenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-one (**35**)[19] in 5 mL of anhydrous ether at 25 °C was added 44 mg of phenylmagnesium bromide. After being stirred for 5 h the clear yellow solution was poured into ice-cold dilute hydrochloric acid, and the mixture was extracted with ether. The combined ether extracts were washed with a saturated salt solution and dried over magnesium sulfate, and then the solvent was removed under reduced pressure to leave behind 75 mg of a colorless oil. This material was purified by silica gel flash chromatography to give 50 mg (56%) of a white crystalline solid whose structure was assigned as 3a,4-dihydro-1-methyl-2,3a-diphenyl-1,4-methano-5*H*-oxazolo[3,2-*a*]quinolin-2(1*H*)-ol (**42**) on the basis of its spectral properties: mp 96–97 °C; IR (KBr) 1600, 1570, 1450, 1380, 1240, 1070, 1018, 908, and 760 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.86 (dd, 1 H, J = 14.0 and 2.0 Hz), 1.25 (s, 3 H), 1.82 (dd, 1 H, J = 14.0 and 7.0 Hz), 2.43 (dd, 1 H, J = 17.0 and 3.0 Hz), 2.72 (dd, 1 H, J = 17.0 and 3.0 Hz), 3.10 (m, 1 H), 4.41 (s, 1 H), 6.7–8.1 (m, 14 H); UV (95% ethanol) 234 nm (ϵ 6830); MS, m/e 369 (M^+), 264, 218, 105 (base); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.8 (q), 34.4 (t), 35.4 (t), 40.7 (d), 79.0 (s), 97.8 (s), 105.1 (s), 126.0 (d), 126.4 (d), 127.2 (d), 127.4 (d), 127.6 (d), 127.8 (d), 128.2 (d), 128.4 (d), 129.6 (d), 130.3 (s), 135.6 (s), 137.2 (s), 142.6 (s). Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.28; N, 3.79. Found: C, 81.13; H, 6.33; N, 3.75.

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Supplementary Material Available: Complete experimental conditions and spectral data are given for the preparation of *N*-formyl-*N*-(*o*-allylphenyl)alanine, *N*-formyl-*N*-(*o*-allylphenyl)-2-phenylglycine, *N*-(*o*-allylphenyl)glycine, *N*-acetyl-*N*-(*o*-allylphenyl)glycine, *N*-benzoyl-*N*-(*o*-allylphenyl)glycine, *N*-formyl-*N*-(*o*-allylphenyl)glycine, *N*-acetyl-*N*-(*o*-vinylbenzyl)glycine, *N*-benzoyl-*N*-(*o*-vinylbenzyl)glycine, *N*-acetyl-*N*-(*o*-vinylbenzyl)alanine, and *N*-benzoyl-*N*-(*o*-vinylbenzyl)alanine (14 pages). Ordering information is given on any current masthead page.