Synthesis of Hydroisoindoles *via* Intramolecular Diels–Alder Reactions of Functionalised Amido Trienes

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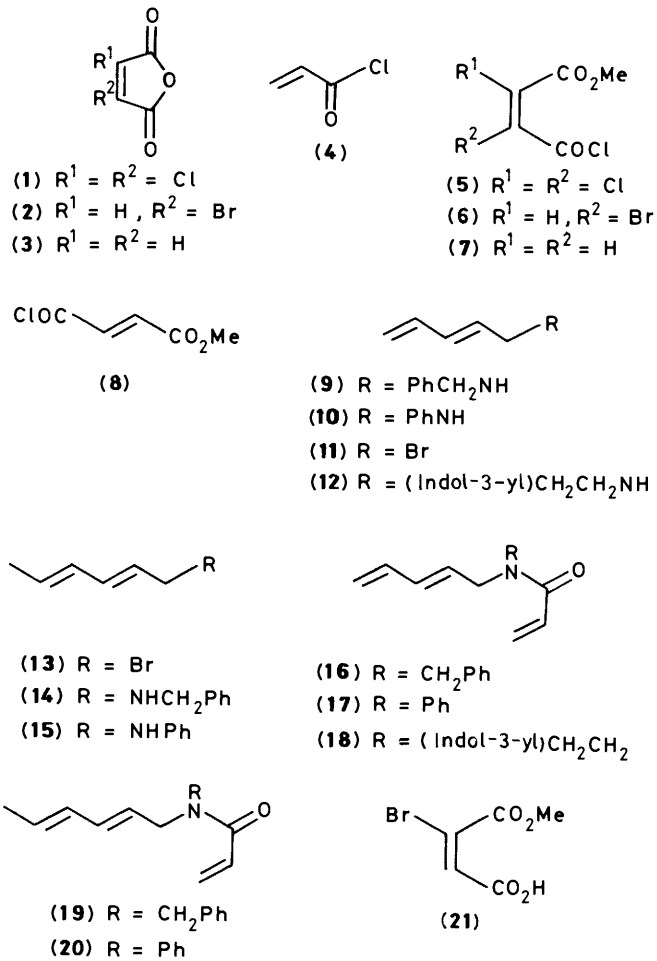
Reactions of amino dienes with acryloyl chloride, maleic anhydride, bromomaleic anhydride, and dichloromaleic anhydride were studied. Acylation and intramolecular reaction by Diels–Alder cyclisation gave bicyclic adducts. Adducts of dichloromaleic anhydride readily underwent dechlorodecarboxylation to give either conjugated or non-conjugated dienes. By studying related cyclisations with other dienophiles, the relative preference for formation of either *cis*- or *trans*-fused bicyclic adducts was determined. The dehydrochlorination, the reductive dechlorination, and the hydrogenation of certain adducts is reported.

The synthesis of cyclic lactams by the intramolecular Diels–Alder (IMDA) reaction is less developed than the construction of carbocycles [1] or lactones [2] by this methodology. However, the cyclisation of amido trienes incorporating simple acrylamide functionality (Scheme; $R^1 = R^2 = R^3 = H$) proceeds readily with,[3] or without,[4,5] metal-ion catalysis. Examples of more

Scheme.

complex systems featuring amides of a type related to fumaric acid [6] derivatives (Scheme; $R^1 = R^3 = H$, $R^2 = CO_2R$) and to maleic acid [7] derivatives (Scheme; $R^1 = CO_2R$, $R^2 = R^3 = H$) are reported to cyclise even more readily. However, whereas in the construction of cyclic lactones by the IMDA reaction of triene esters extra functionality has been introduced into the adducts by suitable choice of more highly functionalised diene or dienophilic units,[8] few such studies have been reported in the construction of lactams. In an approach to the synthesis of a fragment of the avermectins [9] use of a β-chloroacrylamide was made to enable the IMDA adduct to be elaborated *via* a reductive elimination. Following our initial investigation [10] of the IMDA reaction of triene esters incorporating a dienophilic moiety derived from dichloromaleic anhydride (**1**), it was of interest to establish whether extra functionality might be introduced into IMDA adducts of amido trienes derived from the anhydride (**1**) and related compounds. In the previous paper [8] we report our results concerning the synthesis of functionalised lactones from triene esters. In this paper we report the cyclisation of amido trienes derived from both dichloromaleic anhydride (**1**) and bromomaleic anhydride (**2**) and show how the subsequent elaboration of the IMDA adducts permits the synthesis of a variety of functionalised bicyclic lactams. Some preliminary results [11] have been reported.

We describe IMDA reactions based on a variety of both dienophilic partners and dienes. In addition to the halogenomaleic anhydrides (**1**) and (**2**), other dienophiles, including maleic anhydride (**3**), acryloyl chloride (**4**), and the esters (**5**)—(**8**) were studied. As dienes we chose dienylamines derived from aniline, benzylamine, and tryptamine, as it has previously been reported [6] that secondary amides are less reactive than tertiary amides in the IMDA reaction.



Recently [3] the amine (**9**) has been prepared by the alkylation of benzylamine with the known [12] pentadienyl bromide (**11**) using phase-transfer catalysis. We found that the amine (**9**) could be prepared in 43% yield by an alkylation in dimethylformamide (DMF). In a similar manner from the known [13] bromide (**13**) the amine (**14**) was prepared in 43% yield. The required amines (**10**) and (**15**) were prepared by alkylation of aniline in DMF but it was found to be convenient to delay purification of products until after the subsequent acylation. Tryptamine was alkylated to give the dienylamine (**12**) in 22%

Table 1. Cyclisation of amides derived from acryloyl chlorides

Amido triene	Products (Yield %)[a] *cis*-Adduct	*trans*-Adduct	Ratio *cis*:*trans*
(16)	**(26)** 32 **(52)**[b]	**(32)** 34 **(48)**[b]	1:1
(19)	**(27)** 29	**(33)** 28	1:1
(17)	**(28)** 42	**(34)** 29	3:2
(20)	**(29)** 46	**(35)** 21	2:1
(18)	**(30)** 40	**(36)** 42	1:1
(22)[c]		**(37)** 21	0
(25)[c]		**(38)** 41	0
(23)[c]		**(39)** 90	0
(24)	**(31)** 14	**(40)** 73	1:5

[a] Isolated yields after chromatographic separation. [b] Ref. 5: yield determined by h.p.l.c. analysis. [c] Amido triene which is prepared at room temperature undergoes direct cyclisation at this temperature.

Table 2. Cyclisation of amides derived from anhydrides and amino-dienes[a]

Amino diene	Anhydride	Product (Yield %)[b]
(14)[c]	**(1)**	**(41)** 69
(14)	**(1)**	**(42)** 91
(9)	**(1)**	**(44)** 65
(10)	**(1)**	**(45)** 58
(15)	**(1)**	**(43)** 87
(12)	**(1)**	**(46)** 67
(14)[d]	**(2)**	**(47)** 38
(14)	**(3)**	**(48)** 82

[a] Reactions in toluene under reflux. [b] Isolated yields after chromatography or by crystallisation. [c] Reaction in ether 0 °C. [d] Reaction in ether at room temperature.

yield. Acylation of the amines **(9)**, **(10)**, **(12)**, **(14)**, and **(15)** was carried out in pyridine–ether at 0 °C with acryloyl chloride **(4)** and, following work-up and chromatography, the amides **(16)**—**(20)** were isolated in 50—70% yield. Acylation of the amines with the anhydrides is more complex. Typically, at 0 °C, cyclisation of the trienes to give bicyclic adducts is sufficiently fast that the acyclic triene intermediates are not isolated. Further, in the case of adducts of dichloromaleic anhydride **(1)** a subsequent dechlorodecarboxylation of the first formed bicyclic acids could lead to the isolation of non-acidic products. This chemistry of the adducts is discussed later. These complications indicated that products of reaction of the amines with the anhydrides were more easily isolated following the IMDA reaction.

Four substituted acryloyl chlorides **(5)**—**(8)** were prepared by unexceptional methods reported in the Experimental section. Interestingly, the reaction of methanol with bromomaleic anhydride **(2)** gives only the ester **(21)**, from which the acid chloride **(6)** is readily prepared by reaction with oxalyl chloride. From the acid chlorides **(5)**—**(8)** amides were prepared, but again typically cyclisation even at 0 °C was sufficiently fast that products were preferably isolated as the IMDA bicyclic adducts.

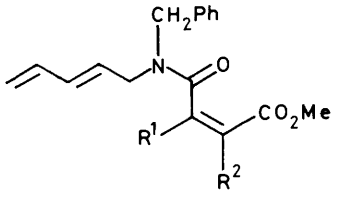
The selective opening, by methanol, of the anhydride **(2)** to give only the ester **(21)** was established by the subsequent nature of the adducts obtained from the acid chloride **(6)**. Later we discuss the selectivity of attack of amines upon the anhydride **(2)** where it is observed that attack occurs at the other carbonyl group from that observed with methanol. The apparent discrepancy of opening the anhydride at two different sites by different nucleophiles has some literature precedent. Thus sorbyl alcohol reacts with citraconic anhydride[14] with no selectivity, yet the same anhydride[14] with sodium methoxide in methanol gives the two possible substituted maleate half-esters in the ratio 8:1. Here it may be concluded that different mechanistic pathways are involved. Similarly, in the study of the reduction of halogenomaleic anhydrides[15] and related unsaturated anhydrides[16] by metal hydrides, whilst a preference for reduction at that carbonyl group α to the halogen substituent has been observed, it is concluded that a number of factors determine the observed selectivity. Hence in the reactions leading to either amides or to esters the difference in selectivity could be explained in a number of ways. We are currently unable to define the origin of our observed selectivities.

From the appropriate acyclic precursors cyclisations were conducted at 0 °C, or in toluene or xylene under reflux. The outcome of IMDA reactions using either acryloyl chloride **(4)** or the substituted acryloyl chlorides **(5)**—**(8)** is shown in Table 1, and reactions based on the use of the anhydrides **(1)**—**(3)** as the dienophilic partners are shown in Table 2. In the reactions described in Table 1 the amido trienes **(16)**—**(20)** were cyclised by heating in xylene but the amido trienes **(22)**, **(23)**, and **(25)** were not isolated as the reaction of the amino diene **(9)** with the acid chlorides **(6)**—**(8)** at room temperature afforded directly the cyclic adducts. The amido triene **(24)** could be isolated and then cyclised by reaction in hot toluene. The adducts **(26)**—**(40)** were isolated by direct crystallisation or following chromatographic separation. As discussed below the reaction described in Table 2 afforded either acids or, after dechlorodecarboxylation, neutral unsaturated lactams as products. The unstable acid **(41)** could be isolated following acylation of the amino diene **(14)** by dichloromaleic anhydride **(1)** at 0 °C. The stable acids **(47)** and **(48)** were isolated after reaction of the amino diene **(14)** with the appropriate anhydrides. The products of dechlorodecarboxylation **(42)**—**(46)** could be isolated following reaction of the appropriate amino dienes with dichloromaleic anhydride **(1)** in hot toluene.

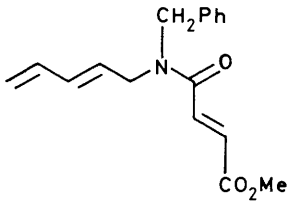
In each of the examples leading to a pair of adducts, shown in Table 1, discrimination between the adducts can be made based on two spectroscopic features. The less strained *cis*-lactams are characterised by $\nu_{max.} \sim 1\,690$ cm^{-1}, whereas the more strained *trans*-lactams are characterised by $\nu_{max.}$ 1 700 cm^{-1}. The magnitudes of the coupling constants $J_{1,9\alpha}$ and $J_{1,9\beta}$ are 3 and 7.5 Hz for the *cis*-fused lactam but 7 and 11 Hz for the *trans*-fused lactam.* The observation of the lack of stereoselectivity in the IMDA reaction of amides derived from acryloyl chloride is in accord with the previously reported examples[6] but contrasts with the other examples in Table 1 based on cyclisation of functionalised acrylamides.

The bromo ester **(23)** under the conditions of formation of the amide undergoes cyclisation to give a single adduct **(39)** in 90% yield. The assignment of the *trans*-fused structure to this adduct **(39)** is based both on observation of the coupling constant $J_{1,6}$ (12.5 Hz), which is indicative of the *trans*-relationship of 1-H and 6-H, and the observation of $J_{1,9\alpha}$ and $J_{1,9\beta}$ (4.5 and 8.5 Hz respectively).* In contrast, the chloro ester **(24)** is sufficiently stable to be easily isolated, but on cyclisation the two adducts **(31)** and **(40)** are obtained. The major, *trans*-fused isomer **(40)** is recognised on the basis of the i.r. data ($\nu_{max.}$ 1 720 cm^{-1} for the more strained lactam carbonyl group) and the *cis*-isomer **(31)** was recognised by coupling constant data ($J_{1,9\alpha}$ 6 Hz and $J_{1,9\beta}$ 0 Hz).* Two interesting features of these cyclisations, both more marked with the triene **(23)**, are the ease with which cycloaddition takes place, and the high stereoselectivity of formation of the *trans*-adducts. This high stereoselectivity has been previously recognised in other cycloadditions of functionalised

* C-9 is the ring carbon α to the lactam nitrogen.



(22) $R^1 = R^2 = H$
(23) $R^1 = H, R^2 = Br$
(24) $R^1 = R^2 = Cl$



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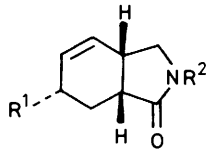
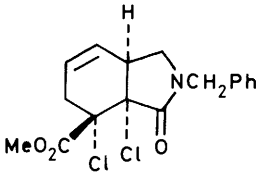


(26) $R^1 = H, R^2 = PhCH_2$
(27) $R^1 = Me, R^2 = PhCH_2$
(28) $R^1 = H, R^2 = Ph$
(29) $R^1 = Me, R^2 = Ph$
(30) $R^1 = H, R^2 = (Indol\text{-}3\text{-}yl)CH_2CH_2$



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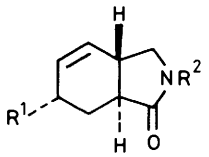
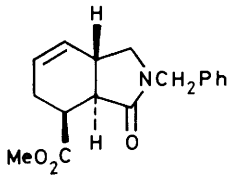


(32) $R^1 = H, R^2 = PhCH_2$
(33) $R^1 = Me, R^2 = PhCH_2$
(34) $R^1 = H, R^2 = Ph$
(35) $R^1 = Me, R^2 = Ph$
(36) $R^1 = H, R^2 = (Indol\text{-}3\text{-}yl)CH_2CH_2$



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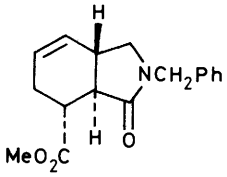

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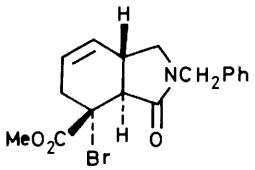

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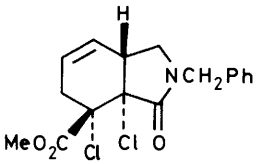

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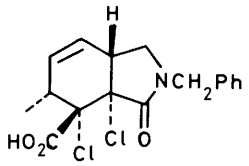
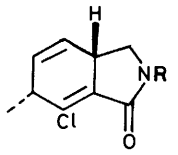
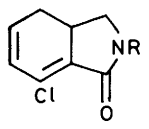


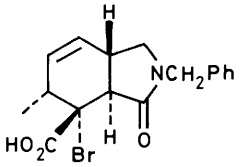
(41)



(42) R = $PhCH_2$
(43) R = Ph



(44) R = $PhCH_2$
(45) R = Ph
(46) R = $(Indol\text{-}3\text{-}yl)CH_2CH_2$



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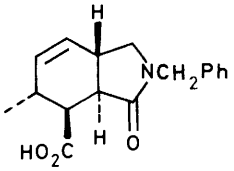


(48)

acrylamides,[6] and is confirmed in our formation of the adducts (37) and (38). Under the conditions of formation of the amides and their subsequent cycloaddition, possible isomerisations of the diene or dienophilic moiety do not occur significantly. Hence dichloromaleic anhydride (1) and bromomaleic anhydride (2) may be used in stereoselective and regiosepecific routes, *via* sequential esterification, amide formation, and IMDA cyclisation to afford functionalised lactams.

In Table 2 conditions are given which lead to the formation of the acids (41), (47), and (48) by direct reaction of the amino dienes with the appropriate anhydrides. Structures can readily be assigned to the acids (47) and (48) by observation of the coupling constant $J_{1,6}$ [$J_{1,6}$ 12.5 Hz for (47) and $J_{1,6}$ 12.5 Hz for (48)] indicative of the *trans*-ring fusion. The probable structure of the acid (41) was assigned by spectral comparisons with the other acids (47) and (48). The similar magnitude of the coupling constants $J_{1,9\alpha}$ and $J_{1,9\beta}$* [8.0 and 7.0 Hz for (41) and 7.5 and 6.0 Hz for (47)] suggest that both acids have the same stereochemistry about the ring junction, *i.e. trans*. Hence direct reaction of amino dienes with the halogenated anhydrides can lead stereospecifically to IMDA adducts.

Although the acid (41) can be isolated, on heating it readily undergoes dechlorodecarboxylation to give an unsaturated lactam (42). This dechlorodecarboxylation is not unexpected as the *trans*-antiperiplanar relationship of the carboxylic acid and vicinal chlorine in the *trans*-fused acid (41) should facilitate reaction. The formation of compound (42) is possible by treating the acid (41) with triethylamine in tetrahydrofuran

* See footnote on p. 998.

(THF) at room temperature, by heating the acid (**41**) under reflux in toluene, or by directly heating the amine (**14**) with dichloromaleic anhydride (**1**) in toluene.

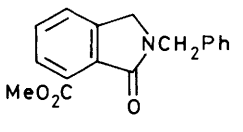
The structure of the product of dechlorodecarboxylation (**42**) is readily assigned from the ^{1}H n.m.r. spectrum. Observation of a methyl resonance as a doublet at δ 1.38 and of the coupling constants $J_{1,9}$ defines the structure.* Dechlorodecarboxylation is not followed by isomerisation. In order to study further the generality of the dechlorodecarboxylation and possible absence of isomerisation, we examined the other cases shown in Table 2.

Reaction of the amino diene (**14**) with dichloromaleic anhydride (**1**) also afforded a non-conjugated diene (**43**). However, reaction of the dienes (**9**), (**10**), and (**12**) with dichloromaleic anhydride (**1**) gave in each case the conjugated dienes (**44**), (**45**), and (**46**) respectively. The conjugated nature of these dienes could be recognised from decoupling experiments. Irradiations established the vicinal relationship between the protons at C-1 and C-2. The non-conjugated diene (**43**) could be recognised by the observation of a doublet at δ 1.38 associated with the C-4 methyl resonance.

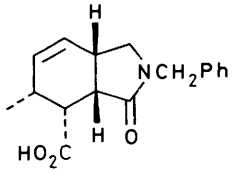
Hence the products of dechlorodecarboxylation are determined by the facility with which isomerisation from a non-conjugated to a conjugated diene occurs. With the extra methyl substituent in the case of the products (**42**) and (**43**) the extra steric hindrance retards isomerisation. The results in Table 2 establish that the combination of IMDA reaction and dechlorodecarboxylation permit an effective synthesis of bicyclic unsaturated lactams from acyclic amido trienes.

Two aspects of the chemistry of the adducts were briefly investigated; their ease of dehydrochlorination, and their reduction using zinc in acetic acid, under conditions of catalytic hydrogenation. In the adducts formed from dichloromaleic anhydride (**1**) the *trans*-antiperiplanar relationship of hydrogen and chlorine about the ring junction should facilitate dehydrochlorination. Treatment of the ester (**40**) with triethylamine in hot THF gave the ester (**49**) in 75% yield. Under less vigorous conditions the starting material was recovered unchanged, and no intermediate corresponding to the loss of one equivalent of hydrogen chloride could be isolated. Under similar conditions the bromo ester (**39**) did not react. This lower reactivity is not unexpected as the conformation of the bicyclic system is likely to place the bromine atom in a pseudo-equatorial position.

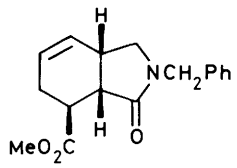
Treatment of the dichloro ester (**40**) and the dichloro acid (**41**) with zinc in acetic acid gave the respective reduction products (**50**) from the acid (**41**), and the mixture of esters (**51**) and (**52**) from the ester (**40**). The recognition in the reduction product (**50**) of a *cis*-ring junction ($\nu_{max.}$ 1 630 cm^{-1}, lowered by hydrogen bonding) and the analysis of coupling-constant data,



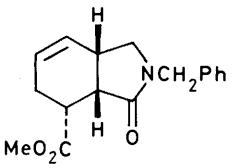
(**49**)



(**50**)



(**51**)

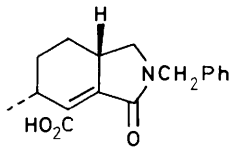


(**52**)

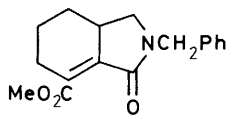
* See footnote on p. 998.

establish the structure of this acid. The esters (**51**) and (**52**) can be separated by chromatography and again their *cis*-ring junctions can be recognised. Assignment of the relative configurations to the epimers (**51**) and (**52**) follows from the close identity of the spectra of the acid (**50**) and the ester (**52**). In formation of products (**50**)—(**52**) reduction from the less hindered face is likely to lead to the *cis*-ring junction which is, in any case, the thermodynamically favoured system. The contrast in the selectivity of the formation of the acid (**50**) rather than an epimeric mixture (1:1) of the esters (**51**) and (**52**) may be explained by the extra difficulty of attack on the α-face, the face of the methyl substituent, in the case of the acid (**50**).

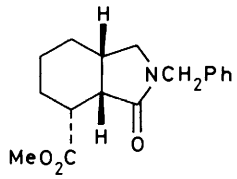
Four examples of catalytic hydrogenation were studied. The acid (**41**) afforded the unsaturated acid (**53**) in 45% yield, but the ester (**40**) gave a separable mixture of the unsaturated and saturated esters (**54**) and (**55**). An examination of the conditions of the latter hydrogenation failed to establish a selective preparation of the unsaturated ester (**54**). Structural assignments are based on the well established criteria of i.r. and coupling-constant data. Although the sequence of mechanistic events leading to the formation of these reduction products is not clear it is interesting to observe some selectivity in formation of the unsaturated systems. Similarly in hydrogenation of the products of dehydrochlorination (**42**) and (**44**) to give, respectively, the unsaturated amides (**56**) and (**57**), satisfactory chemoselectivity is observed.



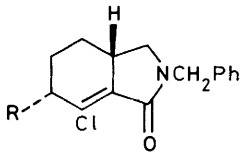
(**53**)



(**54**)



(**55**)



(**56**) R = Me
(**57**) R = H

In the preceding paper,[8] the synthesis and elaboration of halogenated IMDA adducts, lactones derived from halogenated anhydrides, were described. From the results described in this paper we can conclude that a similar methodology is well suited to the synthesis of halogenated lactams. In particular the readily occurring cyclisation of amido trienes, and in the case of acids, the easy dechlorodecarboxylation of acid adducts, makes a route to unsaturated lactams very straightforward. The application of these reactions even to tryptamine derivatives indicates some potential for this methodology in the synthesis of more complex structures.

Experimental

General methods are described in the preceding paper.[8]

Synthesis of Acyclic Precursors from Acryloyl Chloride (**4**).—Preparation of the acrylamide (**16**) has previously been reported[5] from reaction of the bromide (**11**) with benzylamine followed by acylation with acryloyl chloride (**4**). All dienyl compounds reported in this paper are derived from reactions of the known bromides (**11**)[12] and (**13**).[13] Reaction of benzylamine with the bromides (**11**) and (**13**) afforded the amines (**9**)

and (**14**) respectively in 43 and 43% yields. Similarly the unstable amine (**12**) was prepared by reaction of tryptamine with the bromide (**11**), and reaction of aniline with the bromides (**11**) and (**13**) gave the amines (**10**) and (**15**) respectively. Acylation of each of the above amino dienes with acryloyl chloride (**4**) at 0 °C in pyridine–ether followed by work-up and flash chromatography afforded crude amido trienes (50—70% yield). Typically, by acylation at higher temperatures, amino dienes were converted directly *via* intermediate amidotrienes into cyclic adducts.

Intramolecular Diels–Alder Reactions.—(a) *Cyclisations using acryloyl chloride* (**4**) *as a latent dienophile.* A solution of the crude triene, obtained as described above, was heated under reflux in toluene for 18 h. The solution was concentrated under reduced pressure to give a brown oil, which was purified by flash column chromatography [eluant ether–light petroleum (1:1)] to give the following lactams (*cis*-lactams were isolated as the less polar fractions followed by *trans*-lactams as the more polar fractions).

(1RS,6SR)-8-*Phenyl*-8-*azabicyclo*[4.3.0]*non*-2-*en*-7-*one* (**28**) as a white crystalline solid in 42% yield, m.p. 102—103 °C (Found: C, 78.5; H, 7.1; N, 6.5. $C_{14}H_{15}NO$ requires C, 78.8; H, 7.1; N, 6.6%); $\nu_{max.}$($CHCl_3$) 1 690 and 1 600 cm^{-1}; δ_H(360 MHz) 7.6—7.1 (5 H, complex, Ph), 5.89 (1 H, br d, *J* 10.0 Hz, 2- or 3-H), 5.60 (1 H, br d, *J* 10.0 Hz, 3- or 2-H), 3.96 (1 H, dd, *J* 9.0 and 7.5 Hz, 9-H), 3.47 (1 H, dd, *J* 9.0 and 3.0 Hz, 9-H), 2.97 (1 H, m, 1-H), 2.85 (1 H, m, 6-H), and 2.14—1.78 (4 H, complex); δ_C 20.63, 21.59 (CH_2), 31.52, 42.10 (CH), 53.19 (CH_2), 119.85, 124.28, 126.61, 128.77, 130.29 (=CH), 139.90 (C), and 174.93 (C=O) (Found: M^+, 213.1120. $C_{14}H_{15}NO$ requires *M*, 213.1154); *m*/*z* 213 (100%), 106 (85.0), and 77 (13.8).

(1RS,6RS)-8-*Phenyl*-8-*azabicyclo*[4.3.0]*non*-2-*en*-7-*one* (**34**) as a white crystalline solid in 29% yield, m.p. 142—143 °C (Found: C, 78.5; H, 7.1; N, 6.5%); $\nu_{max.}$($CHCl_3$) 1 700 and 1 600 cm^{-1}; δ_H(360 MHz) 7.6—7.1 (5 H, complex, Ph), 5.87 (1 H, dd, *J* 10.0 and 2.0 Hz, 2- or 3-H), 5.75 (1 H, m, 3- or 2-H), 3.80 (1 H, dd, *J* 9.0 and 7.0 Hz, 9-H), 3.49 (1 H, dd, *J* 11.0 and 9.0 Hz, 9-H), 2.65 (1 H, m, 1-H), and 2.33—1.64 (5 H, complex); δ_C 22.14 26.08 (CH_2), 38.83, 47.34 (CH), 51.63 (CH_2), 119.46, 124.00, 125.25, 128.80, 130.17 (=CH or ArC), 140.16 (C), and 174.22 (C=O) (Found: M^+, 213.1120. $C_{14}H_{15}NO$ requires *M*, 213.1154); *m*/*z* 213 (100%), 106 (85.0), and 77 (13.8).

(1RS,6SR)-8-*Benzyl*-8-*azabicyclo*[4.3.0]*non*-2-*en*-7-*one* (**26**) as an oil in 32% yield (Found: M^+, 227.1314. $C_{15}H_{17}NO$ requires *M*, 227.1310); *m*/*z* 227 (59.2%) and 91 (100); $\nu_{max.}$($CHCl_3$) 1 670 and 1 605 cm^{-1}; δ_H(360 MHz) 7.33—7.13 (5 H, complex, Ph), 5.85 (1 H, m, 2- or 3-H), 5.49 (1 H, br d, *J* 8.5 Hz, 3- or 2-H), 4.51 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.34 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.37 (1 H, dd, *J* 9.0 and 7.0 Hz, 9-H), 2.85 (1 H, dd, *J* 9.0 and 6.0 Hz, 9-H), 2.81 (1 H, m, 1-H), 2.70 (1 H, m, 6-H), and 2.07—1.76 (4 H, complex); δ_H 20.52, 21.57 (CH_2), 31.71, 40.54 (CH), 46.32, 51.23 (CH_2), 126.79, 127.25, 127.76, 128.43, 129.51 (=CH), 136.53 (C), and 175.48 (C=O).

(1RS,6RS)-8-*Benzyl*-8-*azabicyclo*[4.3.0]*non*-2-*en*-7-*one* (**32**) as an oil in 34% yield (Found: M^+, 227.1312); *m*/*z* 227 (52.5%) and 91 (100); $\nu_{max.}$($CHCl_3$) 1 680 and 1 605 cm^{-1}; δ_H(360 MHz) 7.30—7.15 (5 H, complex, Ph), 5.75—5.60 (2 H, complex, 2- and 3-H), 4.51 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.34 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.21 (1 H, dd, *J* 9.0 and 7.0 Hz, 9-H), 2.90 (1 H, dd, *J* 10.5 and 9.0 Hz, 9-H), 2.48 (1 H, m, 1-H), and 2.30—1.58 (5 H, complex); δ_C 21.99, 25.95 (CH_2), 39.52, 45.90 (CH), 46.35, 49.40 (CH_2), 125.40, 127.23, 127.79, 128.43, 129.39 (=CH), 136.87 (C), and 174.79 (C=O).

(1RS,4SR,6SR)-4-*Methyl*-8-*phenyl*-8-*azabicyclo*[4.3.0]*non*-2-*en*-7-*one* (**29**) as an oil in 46% yield (Found: M^+, 227.1277. $C_{15}H_{17}NO$ requires *M*, 227.1310); *m*/*z* 227 (100%), 106 (83.6), and 77 (32.2); $\nu_{max.}$($CHCl_3$) 1 695, 1 655, and 1 600 cm^{-1}; δ_H(360 MHz) 7.58—7.10 (5 H, complex, Ph), 5.74 (1 H, d, *J* 10.0 Hz, 2- or 3-H), 5.66 (1 H, ddd, *J* 10.0, 3.0, and 3.0 Hz, 3- or 2-H), 3.90 (1 H, dd, *J* 9.0 and 9.0 Hz, 9-H), 3.51 (1 H, dd, *J* 9.0 and 9.0 Hz, 9-H), 2.92 (1 H, m, 1-H), 2.72 (1 H, ddd, *J* 12.5, 8.0, and 4.5 Hz, 6-H), 2.23—2.06 (3 H, complex), and 1.05 (3 H, d, *J* 7.0 Hz, Me); δ_C 21.41 (Me), 29.21 (CH), 30.03 (CH_2), 31.29, 42.64 (CH), 53.07 (CH_2), 119.13, 124.34, 124.62, 128.75, 136.17 (=CH), 139.64 (C), and 176.00 (C=O).

(1RS,4RS,6RS)-4-*Methyl*-8-*phenyl*-8-*azabicyclo*[4.3.0]*non*-2-*en*-7-*one* (**35**) as an oil in 21% yield (Found: M^+, 227.1179); *m*/*z* 227 (40.9%), 106 (100), and 77 (15.6); $\nu_{max.}$($CHCl_3$) 1 705 and 1 600 cm^{-1}; δ_H(360 MHz) 7.60—7.10 (5 H, complex, Ph), 5.85 (1 H, dd, *J* 9.5 and 1.5 Hz, 2- or 3-H), 5.66 (1 H, ddd, *J* 9.5, 3.5, and 3.5 Hz, 3- or 2-H), 3.81 (1 H, dd, *J* 9.0 and 7.0 Hz, 9-H), 3.49 (1 H, dd, *J* 11.5 and 9.0 Hz, 9-H), 2.56 (2 H, complex, 1- and 4-H), 2.30 (1 H, ddd, *J* 12.5, 12.5, and 3.0 Hz, 6-H), 2.01 (1 H, dd, *J* 13.0 and 3.0 Hz, 5-H), 1.84 (1 H, ddd, *J* 13.0, 12.5, and 7.0 Hz, 5-H), and 1.10 (3 H, d, *J* 7.0 Hz, Me); δ_C 21.92 (Me), 29.17 (CH_2), 30.42, 39.21, 43.95 (CH), 51.55 (CH_2), 119.54, 124.05, 124.36, 128.85, 136.30 (=CH), 140.26 (C), and 174.63 (C=O).

(1RS,4RS,6SR)-8-*Benzyl*-4-*methyl*-8-*azabicyclo*[4.3.0]*non*-2-*en*-7-*one* (**27**) as a white crystalline solid in 29% yield, m.p. 73—75 °C (from ethyl acetate–pentane) (Found: C, 79.4; H, 8.0; N, 5.7. $C_{16}H_{19}NO$ requires C, 79.6; H, 7.9; N, 5.8%); $\nu_{max.}$($CHCl_3$) 1 675 and 1 605 cm^{-1}; δ_H(360 MHz) 7.33—7.21 (5 H, complex, Ph), 5.64 (1 H, br d, *J* 10.0 Hz, 2- or 3-H), 5.53 (1 H, ddd, *J* 10.0, 3.0, and 3.0 Hz, 3- or 2-H), 4.47 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.39 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.34 (1 H, dd, *J* 9.0 and 9.0 Hz, 9-H), 2.89 (1 H, dd, *J* 9.0 and 9.0 Hz, 9-H), 2.78 (1 H, m, 1-H), 2.61 (1 H, ddd, *J* 7.5, 7.5, and 4.5 Hz, 6-H), 2.17 (1 H, m, 4-H), 2.06 (1 H, ddd, *J* 12.5, 4.5, and 4.5 Hz 5-H), 1.14 (1 H, m, 5-H), and 1.01 (3 H, d, *J* 7.0 Hz, Me); δ_C 21.17 (Me), 29.03 (CH_2), 30.12, 31.55, 41.01 (CH), 46.27, 51.02 (CH_2), 124.77, 127.32, 127.87, 128.47, 135.55 (=CH), 136.52 (C), and 176.53 (C=O).

(1RS,4RS,6RS)-8-*Benzyl*-4-*methyl*-8-*azabicyclo*[4.3.0]*non*-2-*en*-7-*one* (**33**) as a white crystalline solid in 28% yield, m.p. 68—70 °C (from ethyl acetate–pentane) (Found: C, 79.4; H, 8.1; N, 5.7%); $\nu_{max.}$($CHCl_3$) 1 680 and 1 605 cm^{-1}; δ_H(360 MHz) 7.32—7.18 (5 H, complex, Ph), 5.69 (1 H, br d, *J* 10.0 Hz, 2- or 3-H), 5.54 (1 H, ddd, *J* 10.0, 3.0, and 3.0 Hz, 3- or 2-H), 4.44 (2 H, s, CH_2Ph), 3.21 (1 H, dd, *J* 9.0 and 7.0 Hz, 9-H), 2.90 (1 H, dd, *J* 10.5 and 9.0 Hz, 9-H), 2.42 (2 H, complex, 1- and 4-H), 2.12 (1 H, ddd, *J* 12.5, 12.5, and 2.5 Hz, 6-H), 1.98 (1 H, dd, *J* 13.0 and 2.5 Hz, 5-H), 1.76 (1 H, ddd, *J* 12.5, 12.5, and 7.0 Hz, 5-H), and 1.05 (3 H, d, *J* 7.0 Hz, Me); δ_C 21.64 (Me), 28.95 (CH_2), 30.15, 39.83, 42.36 (CH), 46.41, 49.23 (CH_2), 124.45, 127.22, 127.80, 128.43, 135.44 (=CH), 136.88 (C), and 175 (C=O).

(1RS,6RS)-8-[2-(*Indol*-3-*yl*)*ethyl*]-8-*azabicyclo*[4.3.0]*non*-2-*en*-7-*one* (**30**) as a white crystalline solid in 40% yield, m.p. 134—138 °C (from ethyl acetate–pentane) (Found: C, 77.0; H, 7.2; N, 10.0. $C_{18}H_{20}N_2O$ requires C, 77.1; H, 7.2; N, 10.0%); $\nu_{max.}$($CHCl_3$) 3 490, 1 680, and 1 620 cm^{-1}; δ_H(360 MHz) 9.07 (1 H, br s, NH-indole), 7.57—7.07 (4 H, complex, ArH), 6.92 (1 H, d, *J* 2.5 Hz, NCH=), 5.77 (1 H, m, 2- or 3-H), 5.43 (1 H, br d, *J* 10.0 Hz, 3- or 2-H), 3.59 (2 H, complex, NCH_2CH_2), 3.37 (1 H, dd, *J* 9.5 and 7.5, 9-H), 2.91 (2 H, complex, NCH_2CH_2), 2.90 (1 H, dd, *J* 9.5 and 7.5 Hz, 9-H), 2.70 (1 H, m, 1-H), 2.60 (1 H, m, 6-H), and 1.9—1.7 (4 H, complex); δ_C 20.66, 21.65, 23.29 (CH_2), 31.90, 40.80 (CH), 43.05, 52.31 (CH_2), 111.34, 118.43, 119.03, 121.70, 122.20, 126.83 (=CH), 127.44 (C), 129.52 (=CH), 136.52 (C), and 175.85 (C=O).

(1RS,6RS)-8-[2-(*Indol*-3-*yl*)*ethyl*]-8-*azabicyclo*[4.3.0]*non*-2-*en*-7-*one* (**36**) as a white crystalline solid in 42% yield, m.p. 172—175 °C (from ethyl acetate–pentane) (Found: C, 76.7; H, 7.1; N, 9.8%); $\nu_{max.}$($CHCl_3$) 3 490, 1 685, and 1 620 cm^{-1}; δ_H(360 MHz) 8.34 (1 H, br s, NH-indole), 7.61—7.12 (4 H, complex, ArH), 7.03 (1 H, d, *J* 2.5 Hz, NCH=), 5.72 (1 H, dd, *J* 10.0 and 2.0 Hz, 2- or 3-H), 5.64 (1 H, m, 3- or 2-H), 3.73 (1 H, ddd, *J* 14.0, 7.5,

and 7.5 Hz, NC*H*HCH$_2$), 3.59 (1 H, ddd, *J* 14.0, 7.0, and 7.0 Hz, NCH*H*CH$_2$), 3.25 (1 H, dd, *J* 9.0 and 7.0 Hz, 9-H), 2.99 (2 H, dd, *J* 7.0 and 7.0 Hz, NCH$_2$C*H*$_2$), 2.97 (1 H, dd, *J* 9.5 and 9.5 Hz, 9-H), and 2.29—1.53 (5 H, complex); δ_C 22.24, 23.84, 26.18 (CH$_2$), 39.96 (CH), 43.23 (CH$_2$), 46.28 (CH), 50.70 (CH$_2$), 111.40, 118.56, 119.24, 121.93, 122.05, 156.66 (=CH), 127.55 (C), 129.61 (=CH), 136.57 (C), and 175.41 (C=O).

(b) *Cyclisation using maleic anhydride* (**3**), *bromomaleic anhydride* (**2**), *or dichloromaleic anhydride* (**1**) *as latent dienophiles.* Reactions were conducted either at room temperature in ether for 15 h, or under reflux in toluene for 18 h. Acid products were isolated by filtration. Products of dechlorodecarboxylation were isolated after flash chromatography. Thus were prepared the following:

(1RS,2SR,3RS,6RS)-8-*Benzyl*-1,2-*dichloro*-3-*methyl*-9-*oxo*-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylic acid* (**41**) by reaction, at room temperature of the diene (**14**) and dichloromaleic anhydride (**1**) in ether; the product was obtained as a white crystalline solid in 69% yield, m.p. 165—167 °C (from ether–pentane) (Found: C, 57.3; H, 4.8; N, 3.85. $C_{17}H_{17}Cl_2NO_3$ requires C, 57.6; H, 4.8; N, 3.9%); $\nu_{max.}$(CHCl$_3$) 1 730 and 1 670 cm^{-1}; δ_H(360 MHz) 11.1 (1 H, br s, CO$_2$H), 7.29 (5 H, complex, Ph), 5.71 (1 H, ddd, *J* 9.5, 3.0, and 3.0 Hz, 4- or 5-H), 5.53 (1 H, d, *J* 9.5 Hz, 5- or 4-H), 4.48 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.46 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.53 (1 H, m, 3-H), 3.35 (1 H, m, 6-H), 3.22 (1 H, dd, *J* 9.0 and 7.0 Hz, 7-H), 3.17 (1 H, dd, *J* 9.0 and 8.0 Hz, 7-H), and 1.5 (3 H, d, *J* 7.0 Hz, Me); δ_C 19.51 (Me), 40.60, 41.50 (CH), 45.60, 46.53 (CH$_2$), 71.74, 74.04 (C), 119.25, 127.33, 127.70, 128.40, 138.80 (=CH), 135.99 (C), and 167.88 and 169.90 (C=O) [Found: *m/z*, (*M*$^+$ − CO$_2$ − Cl) 274.0991. $C_{16}H_{16}{}^{35}ClNO$ requires *m/z*, 274.0999]; *m/z* 274 (17.4%), 273 (93.8), 139 (100), and 91 (88.5).

(1RS,2SR,3SR,6RS)-8-*Benzyl*-2-*bromo*-3-*methyl*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylic acid* (**47**) by reaction, at room temperature for 1 h in ether, of the diene (**14**) and bromomaleic anhydride (**2**); the product was obtained as a white crystalline solid in 38% yield, m.p. 170—171 °C (from ethyl acetate–pentane) (Found: C, 55.7; H, 5.1; N, 3.8. $C_{17}H_{19}BrNO_3$ requires C, 55.9; H, 5.2; N, 3.8%); $\nu_{max.}$(CHCl$_3$) 1 710 and 1 680 cm^{-1}; δ_H(360 MHz) 9.1—7.8 (1 H, br s, CO$_2$H), 7.35—7.20 (5 H, complex, Ph), 5.72—5.60 (2 H, complex, 4- and 5-H), 4.52 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.37 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.25 (1 H, m, 3-H), 3.22 (1 H, dd, *J* 8.0 and 6.0 Hz, 7-H), 2.95 (1 H, m, 6-H), 2.91 (1 H, dd, *J* 8.0 and 7.5 Hz, 7-H), 2.61 (1 H, d, *J* 12.5 Hz, 1-H), and 1.43 (3 H, d, *J* 7.0 Hz, Me); δ_H 20.20 (Me), 38.16, 39.18 (CH), 45.43, 46.22 (CH$_2$), 46.39 (CH), 61.69 (C), 122.94, 126.42, 126.86, 127.67, 132.63 (=CH), 135.98 (C), and 169.55 and 169.87 (C=O).

(1RS,2SR,3RS,6SR)-8-*Benzyl*-3-*methyl*-9-*oxo*-8-*azabicyclo*-[4.3.0]*non*-4-*ene*-2-*carboxylic acid* (**48**) by reaction, in toluene, of the diene (**14**) and maleic anhydride (**3**) and was obtained as needles in 82% yield, m.p. 170—172 °C (from ethyl acetate–pentane) (Found: C, 71.9; H, 6.3; N, 5.1. $C_{17}H_{18}NO_3$ requires C, 71.8; H, 6.3; N, 4.9%); $\nu_{max.}$(CHCl$_3$) 2 800—2 400, 1 705, and 1 685 cm^{-1}; δ_H(360 MHz) 10.7 (1 H, s, CO$_2$H), 7.25 (5 H, complex, Ph), 5.73 (1 H, d, *J* 10.0 Hz, 4- or 5-H), 5.56 (1 H, ddd, *J* 10.0, 3.0, and 3.0 Hz, 5- or 4-H), 4.50 (2 H, s, C*H*$_2$Ph), 3.30 (1 H, dd, *J* 7.0 and 7.0 Hz, 7-H), 3.06 (1 H, d, *J* 3.5 Hz, 2-H), 2.94 (3 H, complex, 3-, 6-, and 7-H), 2.34 (1 H, dd, *J* 12.5 and 3.5 Hz, 1-H), and 1.17 (3 H, d, *J* 7.0 Hz, Me); δ_C 21.97 (Me), 33.61, 34.57, 43.33, 44.41 (CH), 46.94, 49.44 (CH$_2$), 124.72, 127.62, 128.07, 128.78, 134.18 (=CH), 136.48 (C), and 174.74 and 175.63 (C=O).

(1RS,4SR)-8-*Benzyl*-5-*chloro*-4-*methyl*-8-*azabicyclo*[4.3.0]-*nona*-2,5-*dien*-7-*one* (**42**) by reaction in toluene, of the diene (**14**) and dichloromaleic anhydride (**1**), and was obtained as an oil in 91% yield (Found: *M*$^+$, 273.0907. $C_{16}H_{16}{}^{35}ClNO$ requires *M*, 273.0920); *m/z* 273 (39.6%) and 91 (100); $\nu_{max.}$(CHCl$_3$) 1 690 and 1 605 cm^{-1}; δ_H(360 MHz) 7.35—7.25 (5 H, complex, Ph), 5.66 (2 H, complex, 2- and 3-H), 4.66 (1 H, d, *J* 14.5 Hz, C*H*HPh), 4.35 (1 H, d, *J* 14.5 Hz, C*H*HPh), 3.44 (1 H, m, 1-H), 3.38 (1 H, dd, *J* 8.5 and 8.5 Hz, 9-H), 3.11 (1 H, m, 4-H), 2.93 (1 H, dd, *J* 8.5 and 8.5 Hz 9-H), and 1.38 (3 H, d, *J* 7.0 Hz, Me); δ_C 19.50 (Me), 37.76, 38.65 (CH), 46.93, 49.04 (CH$_2$), 122.67, 127.64, 128.31, 128.72, 132.52 (=CH), 133.67, 135.78, 136.46 (C), and 165.13 (C=O).

The diene (**42**) was also prepared by dechlorodecarboxylation of the acid (**41**) under the following conditions.

Method 1. (1*RS*,2*SR*,3*RS*,6*RS*)-8-Benzyl-1,2-dichloro-3-methyl-9-oxo-8-azabicyclo[4.3.0]non-4-ene-2-carboxylic acid (**41**) (0.10 g, 0.3 mmol) was heated under reflux in dry toluene (15 ml) for 6 h. After cooling, the mixture was concentrated under reduced pressure to yield a deep red oil. The residue was purified by flash chromatography (eluant, ether–light petroleum, 1:1) to afford compound (**42**) (0.064 g, 83%) as an oil.

Method 2. A solution of (1*RS*,2*SR*,3*RS*,6*RS*)-8-benzyl-1,2-dichloro-3-methyl-9-oxo-8-azabicyclo[4.3.0]non-4-ene-2-carboxylic acid (**41**) (0.10 g, 0.3 mmol, 1 mol equiv.) and triethylamine (0.03 g, 0.3 mmol, 1 mol equiv.) was stirred at room temperature in dry THF (10 ml) for 24 h. The THF was removed under reduced pressure and the resulting crude material was dissolved in ether. The ether layer was washed successively with dil. hydrochloric acid and water, dried (MgSO$_4$), and concentrated under reduced pressure to yield compound (**42**) (0.07 g, 91%) as an oil.

(1RS,4SR)-5-*Chloro*-4-*methyl*-8-*phenyl*-8-*azabicyclo*[4.3.0]-*nona*-2,5-*dien*-7-*one* (**43**) by reaction in toluene, of the diene (**15**) and dichloromaleic anhydride (**1**), and was obtained in 87% yield as a pale brown crystalline solid, m.p. 99—101 °C (from ethyl acetate–pentane) (Found: C, 69.0; H, 5.3; N, 5.3. $C_{15}H_{14}ClNO$ requires C, 69.4; H, 5.4; N, 5.4%); $\nu_{max.}$(CHCl$_3$) 1 690 and 1 605 cm^{-1}; δ_H(360 MHz) 7.67—7.25 (5 H, complex, Ph), 5.83 (1 H, ddd, *J* 9.5, 2.0, and 2.0 Hz, 2- or 3-H), 5.74 (1 H, ddd, *J* 9.5, 2.0, and 2.0 Hz, 3- or 2-H), 3.91 (1 H, dd, *J* 8.0 and 8.0 Hz, 9-H), 3.60 (1 H, m, 1-H), 3.54 (1 H, dd, *J* 9.5 and 8.0 Hz, 9-H), 3.18 (1 H, m, 4-H), and 1.40 (3 H, d, *J* 7.5 Hz, Me); δ_C 20.07 (Me), 38.31, 38.46 (CH), 51.08 (CH$_2$), 120.08, 122.61, 125.07, 129.23, 133.25 (=CH), 134.77, 138.0, 140.0 (C), and 164.6 (C=O).

8-*Benzyl*-5-*chloro*-8-*azabicyclo*[4.3.0]*nona*-3,5-*dien*-7-*one* (**44**) by reaction of the diene (**9**) in toluene and was obtained as an oil in 65% yield (Found: *M*$^+$, 259.0749. $C_{15}H_{14}{}^{35}ClNO$ requires *M*, 259.0764); *m/z* 261 (7.5%), 259 (33.2), and 91 (100); $\nu_{max.}$(CHCl$_3$) 1 690, 1 640, and 1 605 cm^{-1}; δ_H (360 MHz) 7.27 (5 H, complex, Ph), 5.74 (2 H, complex 3- and 4-H), 4.61 (1 H, d, *J* 14.5 Hz, C*H*HPh), 4.39 (1 H, d, *J* 14.5 Hz, CH*H*Ph), 3.43 (1 H, m, 1-H), 3.41 (1 H, dd, *J* 8.5 and 7.5 Hz, 9-H), 3.15 (1 H, dd, *J* 22.5 and 11.0 Hz, 2-H$_\beta$), 2.98 (1 H, d, *J* 22.5 Hz, 2-H$_\alpha$), and 2.93 (1 H, dd, *J* 8.5 and 8.0 Hz, 9-H); δ_C 36.69 (CH$_2$), 37.96 (CH), 46.75, 49.37 (CH$_2$), 124.22, 125.48 (=CH), 127.01 (C), 127.64 (=CH), 128.26, 128.72 (=CH), 130.47, 136.43 (C), and 165.02 (C=O).

5-*Chloro*-8-*phenyl*-8-*azabicyclo*[4.3.0]*nona*-3,5-*dien*-7-*one* (**45**) by reaction in toluene, of the diene (**10**) and dichloromaleic anhydride in 58% yield, and was obtained as a pale pink crystalline solid, m.p. 132—134 °C (from ethyl acetate–pentane) (Found: C, 68.2; H, 4.9; N, 5.5. $C_{14}H_{12}ClNO$ requires C, 68.4; H, 4.9; N, 5.7%); $\nu_{max.}$(CHCl$_3$) 1 695, 1 640, and 1 600 cm^{-1}; δ_H(360 MHz) 7.62—7.09 (5 H, complex, Ph), 5.82 (2 H, complex, 3- and 4-H), 3.89 (1 H, dd, *J* 8.0 and 8.0 Hz, 9-H), 3.54 (1 H, m, 1-H), 3.48 (1 H, dd, *J* 9.5 and 8.0 Hz, 9-H), 3.18 (1 H, dd, *J* 22.5 and 12.0 Hz, 2-H), and 3.00 (1 H, dd, *J* 22.5, 7.0, and 4.0 Hz, 2-H); δ_C 36.80 (CH$_2$), 37.36 (CH), 50.90 (CH$_2$), 119.61, 123.86, 124.55, 125.70 (=CH), 127.34 (C), 128.74 (=CH), 131.89, 139.46 (C), and 163.79 (C=O) (Found: *M*$^+$, 245.0602. $C_{14}H_{12}{}^{35}ClNO$ requires *M*, 245.0607); *m/z* 247 (0.7%), 245 (2.1), and 77 (87.9).

5-*Chloro*-8-[2-(*indol*-3-*yl*)*ethyl*]-8-*azabicyclo*[4.3.0]*nona*-3,5-*dien*-7-*one* (**46**) by reaction, in toluene of the diene (**12**)

and dichloromaleic anhydride in 67% yield, and was obtained as a pale pink crystalline solid, m.p. 168—170 °C (from ethyl acetate–pentane) (Found: C, 68.8; H, 5.55; N, 8.7. $C_{18}H_{17}ClN_2O$ requires C, 69.1; H, 5.5; N, 8.9%); $\nu_{max.}$($CHCl_3$) 3 480, 1 695, and 1 680 cm^{-1}; δ_H(360 MHz) 9.15 (1 H, br s, NH-indole), 7.56—7.02 (4 H, complex, ArH), 6.99 (1 H, s, NCH=C), 5.67 (2 H, complex, 3- and 4-H), 3.73 (1 H, ddd, *J* 14.0, 7.5, and 7.5 Hz, C*H*HN), 3.52 (1 H, ddd, *J* 14.0, 7.5, and 7.5 Hz, CH*H*N), and 3.33—2.88 (7 H, complex); δ_C 23.48, 36.56 (CH_2), 38.04 (CH), 43.51, 50.34 (CH_2), 111.37 (=CH), 112.31 (C), 118.40, 119.01, 121.67, 122.12, 124.16, 125.35 (=CH), 127.5, 128.5, 129.71, 136.8 (C), and 165.06 (C=O).

(c) *Cyclisations using the esters* (**22**)—(**25**). A solution of methyl hydrogen dichloromaleate in dry benzene was added dropwise to an excess of oxalyl chloride in benzene and the solution was kept at 50 °C for 2 h. Evaporation under reduced pressure afforded (*Z*)-methyl-2,3-dichloro-3-chloroformylacrylate (**5**) as a liquid in 97% yield.

Similarly (*E*)-methyl 2-bromo-3-carboxyacrylate (**21**), prepared by reaction of methanol with bromomaleic anhydride (**2**), on treatment with oxalyl chloride afforded (*E*)-methyl 2-bromo-3-chloroformylacrylate (**6**) as a liquid.

(*Z*)-Methyl 3-chloroformylacrylate (**7**) was similarly prepared by reaction of methanol with maleic anhydride (**3**), followed by reaction with oxalyl chloride.

(*E*)-Methyl 3-chloroformylacrylate (**8**) was prepared by reaction of fumaroyl chloride with methanol (1 mol equiv.) in dichloromethane.

(1RS,2SR,6SR)-*Methyl* 8-*Benzyl*-1,2-*dichloro*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**31**) *and* (1RS,2SR,6RS)-*Methyl* 8-*Benzyl*-1,2-*dichloro*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**40**).—To a solution of (*E*)-*N*-benzylpenta-2,4-dienylamine (**9**) (0.10 g, 0.58 mmol, 1 mol equiv.) and pyridine (0.09 g, 1.16 mmol, 2 mol equiv.) in ether (10 ml) at 0 °C was added dropwise a solution of (*Z*)-methyl 2,3-dichloro-3-chloroformylacrylate (**5**) (0.15 g, 0.69 mmol, 1.2 mol equiv.) in ether (5 ml). The resulting solution was stirred at room temperature for 24 h, then poured into water, and extracted with ethyl acetate. The combined extract was washed successively with saturated aqueous copper sulphate and water, dried ($MgSO_4$), and concentrated under reduced pressure to yield a pink oil. The residue was purified by flash column chromatography (eluant, ether) to yield (*Z*)-methyl *N*-benzyl-*N*-3-{[(*E*)-penta-2,4-dienyl]carbamoyl}-2,3-dichloroacrylate (**24**) (0.12 g, 56%) as an oil, $\nu_{max.}$($CHCl_3$) 1 745, 1 650, and 1 600 cm^{-1}; δ_H(60 MHz) 7.3 (5 H, s, Ph), 6.8—5.0 (5 H, complex, olefinic), 4.5 (2 H, s, CH_2Ph), 3.85 (3 H, s, OMe), and 3.75 (2 H, d, *J* 7.0 Hz, CH_2N).

Compound (**24**) (1.15 g) was heated under reflux in toluene (50 ml) in the presence of a trace of hydroquinone for 24 h. After cooling, the excess of toluene was removed under reduced pressure to yield a crude yellow oil. Purification was achieved by flash column chromatography (eluant, light petroleum–ether, 1:1) to afford *compound* (**31**) (0.84 g, 73%) as needles, m.p. 104—106 °C (from ethyl acetate–light petroleum) and compound (**40**) (0.16 g, 14%) as an oil.

For compound (**31**) (Found: C, 57.4; H, 4.8; N, 3.8. $C_{17}H_{17}Cl_2NO_3$ requires C, 57.6; H, 4.8; N, 3.95%); $\nu_{max.}$($CHCl_3$) 1 745 and 1 720 cm^{-1}; δ_H(360 MHz) 7.35—7.27 (5 H, complex, Ph), 5.68 (1 H, m, 4- or 5-H), 5.56 (1 H, m, 5- or 4-H), 4.55 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.46 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.82 (3 H, s, OMe), 3.40 (1 H, dm, *J* 19.0 Hz, 3-H), 3.24 (2 H, d, *J* 8.0 Hz, 7-H_2), 3.14 (1 H, m, 6-H), and 2.91 (1 H, ddd, *J* 19.0, 6.0, and 3.0 Hz, 3-H); δ_C 40.20 (CH_2), 42.18 (CH), 45.88, 46.89 (CH_2), 53.81 (OMe), 67.51, 73.22 (C), 116.09, 121.17, 127.69, 127.79, 128.75 (=CH), 136.14 (C), 167.75 and 168.24 (C=O) [Found: *m/z* (M^+ − Cl) 318.0920. $C_{17}H_{17}{}^{35}ClNO_3$ requires *m/z* 318.0897]; *m/z* 318 (8.9%), 281 (36.7), 221 (43.3), and 91 (100).

For compound (**40**) (Found: M^+, 353.0583. $C_{17}H_{17}{}^{35}Cl_2NO_3$ requires *M*, 353.0587); *m/z* (chemical ionisation with isobutane) 354 (100%), 282 (82.9), and 91 (20.0); $\nu_{max.}$($CHCl_3$) 1 740, and 1 710 cm^{-1}; δ_H(360 MHz) 7.32—7.15 (5 H, complex, Ph), 5.77 (1 H, m, 4- or 5-H), 5.53 (1 H, ddd, *J* 10.0, 3.0, and 3.0 Hz, 5- or 4-H), 4.47 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.38 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.90 (3 H, s, OMe), 3.74 (1 H, dd, *J* 10.0 and 6.0 Hz, 7-H), 3.22 (1 H, br d, *J* 3.0 Hz, 6-H), 3.12 (1 H, ddd, *J* 19.0, 3.0, and 3.0 Hz, 3-H), 2.94 (1 H, dd, *J* 19.0 and 6.0 Hz, 3-H), and 2.91 (1 H, d, *J* 10.0 Hz, 7-H_β); δ_C 35.80 (CH_2), 45.14 (CH), 47.07, 49.33 (CH_2), 53.26 (OMe), 66.64, 72.52 (C), 124.42, 125.88, 127.93, 127.96, 128.81 (=CH), 135.19 (C), and 164.74 and 167.90 (C=O).

(1RS,2SR,6RS)-*Methyl* 8-*Benzyl*-2-*bromo*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**39**).—To a cooled solution of (*E*)-*N*-benzylpenta-2,4-dienylamine (**9**) (0.20 g, 1.2 mol, 1 mol equiv.) in ether (20 ml) and pyridine (0.19 g, 2.4 mmol, 2 mol equiv.) was added (*E*)-methyl-2-bromo-3-chloroformylacrylate (**6**) dropwise at such a rate as to maintain the reaction temperature in the range 0—5 °C. The reaction mixture was allowed to warm to room temperature, stirred for 18 h, and then poured into ice–water. The mixture was extracted with ethyl acetate. The combined extracts were washed successively with 10% aqueous copper sulphate and water, dried ($MgSO_4$), and concentrated under reduced pressure to yield a pale yellow oil. Purification was achieved by flash column chromatography (eluant, ether) to give (1RS,2SR,6RS)-*methyl* 8-*benzyl*-2-*bromo*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**39**) as a crystalline solid (0.38 g, 90%), m.p. 81—83 °C (from ethyl acetate–pentane) (Found: C, 56.2; H, 5.0; N, 3.75. $C_{17}H_{18}BrNO_3$ requires C, 56.1; H, 5.0; N, 3.8%); $\nu_{max.}$($CHCl_3$) 1 740 and 1 705 cm^{-1}; δ_H(360 MHz) 7.4—7.2 (5 H, complex, Ph), 5.76 (1 H, m, 4- or 5-H), 5.55 (1 H, m, 5- or 4-H), 4.63 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.36 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.80 (3 H, s, OMe), 3.48 (1 H, ddd, *J* 16.5, 4.0, and 2.0 Hz, 3-H), 3.24 (1 H, dd, *J* 8.5 and 6.5 Hz, 7-H), 2.95—2.70 (3 H, complex, 3-, 6-, and 7-H), and 2.71 (1 H, d, *J* 12.5 Hz, 1-H); δ_C 38.23 (CH), 42.87, 46.56, 47.47 (CH_2), 52.00 (CH), 53.14 (OMe), 53.20 (C), 125.20, 127.52, 127.61, 128.04, 128.65 (=CH), 136.89 (C), and 169.57 and 169.82 (C=O).

(1RS,2SR,6SR)-*Methyl* 8-*Benzyl*-9-*oxo*-8-*azabicyclo*[4.3.0]-*non*-4-*ene*-2-*carboxylate* (**37**).—To a solution of (*E*)-*N*-benzylpenta-2,4-dienylamine (**9**) (0.20 g, 1.2 mmol, 1.1 mol equiv.) in ether (10 ml) at 0 °C was added (*Z*)-methyl 3-chloroformylacrylate (7) (0.19 g, 0.13 mmol, 1.1 mol equiv.) dropwise at such a rate as to maintain the reaction temperature in the range 0—5 °C. The reaction mixture was allowed to warm to room temperature, stirred for 15 h, and then poured into ice–water. The mixture was extracted with ethyl acetate. The combined extracts were washed successively with 10% aqueous copper sulphate and water, dried ($MgSO_4$), and concentrated under reduced pressure to yield a deep red oil. Purification was achieved by flash column chromatography to afford (1RS,2SR,6SR)-*methyl* 8-*benzyl*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**37**) (0.68 g, 21%) as a white crystalline solid, m.p. 71—72 °C (from ethyl acetate–pentane) (Found: M^+, 282.1382. $C_{17}H_{19}NO_3$ requires *M*, 285.1366); *m/z* 285 (40.0%), 225 (9.6), and 91 (100); $\nu_{max.}$($CHCl_3$) 1 730 and 1 690 cm^{-1}; δ_H(360 MHz) 7.35—7.30 (5 H, complex, Ph), 5.78 (1 H, br d, *J* 10.0 Hz, 5-H), 5.65 (1 H, m, 4-H), 4.56 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.41 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.72 (3 H, s, OMe), 3.39 (1 H, dd, *J* 8.0 and 3.5 Hz, 7-H), 3.30 (1 H, m, 7-H), 2.92 (2 H, complex, 1- and 2-H), 2.70 (1 H, dd, *J* 19.0 and 2.0 Hz, 3-H),

2.48 (1 H, m, 3-H), and 2.32 (1 H, dd, *J* 13.5 and 13.5 Hz, 6-H); δ_C 28.85 (CH_2), 34.23, 36.19 (CH), 46.58 (CH_2), 47.04 (CH), 49.11 (CH_2), 51.82 (OMe), 126.04, 127.46, 127.69, 127.93, 128.65 (=CH), 136.98 (C), and 173.00 and 173.35 (C=O).

(1RS,2RS,6SR)-*Methyl* 8-*Benzyl*-9-*oxo*-8-*azabicyclo*[4.3.0]-*non*-4-*ene*-2-*carboxylate* (**38**).—To a solution of (*E*)-*N*-benzylpenta-2,4-dienylamine (**9**) (0.20 g, 1.2 mmol, 1 mol equiv.) was added (*E*)-methyl 3-chloroformylacrylate (**8**) (0.19 g, 0.13 mmol, 1.1 mol equiv.) dropwise at such a rate as to maintain the reaction temperature between 0—5 °C. The reaction mixture was allowed to warm to room temperature, stirred for 15 h, and then poured onto ice–water. The combined extracts were washed successively with 10% aqueous copper sulphate and water, dried ($MgSO_4$), and concentrated under reduced pressure to yield a deep red oil. Purification was achieved by flash column chromatography to yield (1RS,2RS,6SR)-*methyl*-8-*benzyl*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**38**) (0.14 g, 41%) as an oil (Found: M^+, 285.1367. $C_{17}H_{19}NO_3$ requires *M*, 285.1366); *m/z* 285 (66.3%), 225 (19.2), and 91 (100); $\nu_{max.}$($CHCl_3$) 1 735 and 1 690 cm^{-1}; δ_H(360 MHz) 7.3—7.2 (5 H, complex, Ph), 5.77 (1 H, br d, *J* 10.0 Hz, 4- or 5-H), 5.67 (1 H, ddd, *J* 10.0, 6.0, and 3.0 Hz, 5- or 4-H), 4.48 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.37 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.80 (3 H, s, OMe), 3.26 (1 H, dd, *J* 9.0 and 6.5 Hz, 7-H), 2.97 (1 H, dd, *J* 11.0 and 9.0 Hz, 7-H), 2.83 (1 H, ddd, *J* 11.0, 10.5, and 7.0 Hz, 2-H), and 2.6—2.4 (4 H, complex, 1- and 6-H and 3-H_2); δ_C 30.46 (CH_2), 38.80, 40.57 (CH), 46.54 (CH_2), 47.39 (CH), 49.19 (CH_2), 51.81 (OMe), 125.37, 127.52, 127.98, 128.08, 128.65 (=CH), 136.73 (C), and 172.78 and 174.69 (C=O).

Transformation of Adducts.—(a) *Dehydrochlorination. Methyl* N-*benzyl*-2,3-*dihydro*-3-*oxo*-1H-*isoindole*-4-*carboxylate* (**49**). To a solution of (1*RS*,2*SR*,6*SR*)-methyl 8-benzyl-1,2-dichloro-9-oxo-8-azabicyclo[4.3.0]non-4-ene-2-carboxylate (**31**) (0.11 g) in THF (5 ml) was added a large excess of triethylamine. The mixture was heated under reflux for 2 h during which time a white precipitate formed. After cooling, the excess of THF was removed under reduced pressure and the residue was dissolved in ether. The ethereal solution was washed successively with dil. hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and concentrated under reduced pressure to afford *methyl* N-*benzyl*-2,3-*dihydro*-3-*oxo*-1H-*isoindole*-4-*carboxylate* (**49**) (65 mg, 75%) as needles, m.p. 92—94 °C (from ethyl acetate–pentane) (Found: C, 72.5; H, 5.3; N, 4.9. $C_{17}H_{15}NO_3$ requires C, 72.6; H, 5.4; N, 5.0%); $\nu_{max.}$($CHCl_3$) 1 735 and 1 690 cm^{-1}; δ_H(360 MHz) 7.62 (1 H, d, *J* 9.0 Hz, ArH), 7.54 (1 H, dd, *J* 9.0 and 9.0 Hz, ArH), 7.47 (1 H, d, *J* 9.0 Hz, ArH), 7.31 (5 H, complex, Ph), 4.78 (2 H, s, CH_2Ph), 4.25 (2 H, s, 1-H_2), and 4.03 (3 H, s, OMe); δ_H 46.65, 49.15 (CH_2), 52.70 (Me), 116.22, 125.08, 127.83 (ArC), 127.85 (C), 128.39, 128.89 (ArC), 130.82 (C), 131.04 (ArC), 136.87, 142.27 (C), and 166.32 and 167.78 (C=O).

(b) *Dechlorination.* (1RS,2SR,3SR,6RS)-8-*Benzyl*-3-*methyl*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylic acid* (**50**). A mixture of (1*RS*,2*SR*,3*RS*,6*RS*)-8-benzyl-1,2-dichloro-3-methyl-9-oxo-8-azabicyclo[4.3.0]non-4-ene-2-carboxylic acid (**41**) (0.10 g, 0.3 mmol, 1 mol equiv.) and freshly activated zinc dust (0.09 g, 1.4 mmol, 5 mol equiv.) in acetic acid (3 ml) was stirred at room temperature for 18 h. The zinc was filtered off and the filtrate was poured into water. The aqueous layer was extracted with dichloromethane and the combined extracts were washed successively with dil. aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and concentrated under reduced pressure to give an oil. The residue was purified by flash column chromatography (eluant, ether) to yield (1RS,2SR,3SR,-6RS)-8-*benzyl*-3-*methyl*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylic acid* (**50**) (0.05 g, 69%) as an oil (Found: M^+, 285.1351. $C_{17}H_{19}NO_3$ requires *M*, 285.1365); *m/z* 285 (6.4%), 240 (18.9), and 91 (100); $\nu_{max.}$($CHCl_3$) 2 800—2 400, 1 725, and 1 630 cm^{-1}; δ_H(360 MHz) 7.4—7.2 (6 H, complex, Ph and CO_2H), 5.92 (1 H, ddd, *J* 10.0, 5.0, and 2.0 Hz, 4- or 5-H), 5.37 (1 H, ddd, *J* 10.0, 2.0, and 2.0 Hz, 5- or 4-H), 4.60 (1 H, d, *J* 14.5 Hz, C*H*HPh), 4.37 (1 H, d, *J* 14.5 Hz, CH*H*Ph), 3.56 (1 H, dd, *J* 10.0 and 7.0 Hz, 7-H_β), 3.28 (1 H, dd, *J* 7.5 and 4.5 Hz, 1-H), 3.20 (1 H, dd, *J* 6.0 and 4.5 Hz, 2-H), 3.06 (1 H, d, *J* 10.0 Hz, 7-H_α), 3.00 (1 H, m, 6-H), 2.77 (1 H, m, 3-H), and 1.15 (3 H, d, *J* 7.0 Hz, Me).

(1RS,2RS,6RS)-*Methyl* 8-*benzyl*-9-*oxo*-8-*azabicyclo*[4.3.0]-*non*-4-*ene*-2-*carboxylate* (**51**) *and* (1RS,2SR,6RS)-*methyl* 8-*benzyl*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-4-*ene*-2-*carboxylate* (**52**). A solution of (1*RS*,2*SR*,6*SR*)-methyl 8-benzyl-1,2-dichloro-9-oxo-8-azabicyclo[4.3.0]non-4-ene-2-carboxylate (**31**) (0.20 g, 0.56 mmol, 1 mol equiv.) in acetic acid (5 ml) was stirred with freshly activated zinc dust (0.16 g, 2.80 mmol, 5 mol equiv.) for 15 h. The zinc was removed by filtration and the filtrate was poured into ice–water and extracted with dichloromethane. The combined extracts were washed successively with saturated aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and concentrated to yield an oil. Purification was achieved by flash column chromatography (eluant, ether–light petroleum, 1:1) to afford *compounds* (**51**) (86 mg, 36%) and (**52**) (92 mg, 38%) both as oils.

For compound (**51**) (Found: M^+, 285.1368. $C_{17}H_{19}NO_3$ requires *M*, 285.1366); *m/z* 285 (68.4%), 225 (23.7), and 91 (100); $\nu_{max.}$($CHCl_3$) 1 730 and 1 690 cm^{-1}; δ_H(360 MHz) 7.35—7.10 (5 H, complex, Ph), 5.79 (1 H, m, 4- or 5-H), 5.48 (1 H, br d, *J* 10.0 Hz, 5- or 4-H), 4.53 (1 H, d, 15.0 Hz, C*H*HPh), 4.34 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.69 (3 H, s, OMe), 3.44 (1 H, dd, *J* 9.5 and 7.0 Hz, 7-H_α), 3.24 (1 H, m, 2-H), 3.19 (1 H, dd, *J* 7.5 and 3.5 Hz, 1-H), 2.97 (1 H, m, 8-H), 2.86 (1 H, dd, *J* 9.5 and 1.5 Hz, 7-H_β), 2.45 (1 H, dm, *J* 18.0 Hz, 3-H), and 2.27 (1 H, dddd, *J* 18.0, 5.5, 5.5, and 3.0 Hz, 3-H); δ_C 23.45 (CH_2), 30.53, 37.15, 42.40 (CH), 48.51, 51.20 (CH_2), 51.89 (OMe), 127.06, 127.38, 127.47, 127.81, 128.59 (=CH), 136.29 (C), and 173.78 and 174.51 (C=O).

For compound (**52**) (Found: M^+, 285.1368); *m/z* 285 (48.1%), 225 (21.2), and 91 (100); $\nu_{max.}$($CHCl_3$) 1 740 and 1 695 cm^{-1}; δ_H (360 MHz) 7.3—7.1 (5 H, complex, Ph), 5.86 (1 H, m, 4- or 5-H), 5.45 (1 H, dd, *J* 10.0 and 1.5 Hz, 5- or 4-H), 4.53 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.25 (1 H, d, *J* 15.0 Hz, CH*H*Ph), 3.78 (3 H, s, OMe), 3.46 (1 H, dd, *J* 7.5 and 4.0 Hz, 1-H), 3.44 (1 H, dd, *J* 9.5 and 6.5 Hz, 7-H), 2.98 (1 H, m, 6-H), 2.86 (1 H, d, *J* 9.5 Hz, 7-H_β), 2.70 (1 H, ddd, *J* 10.5, 6.5, and 4.5 Hz, 2-H), and 2.43—2.29 (2 H, complex, 3-H_2); δ_C 23.05 (CH_2), 33.49, 37.73, 42.86 (CH), 46.42, 51.12 (CH_2), 51.82 (OMe), 127.33, 127.48, 127.98, 128.35, 128.58 (=CH), 136.33 (C), and 172.94 and 173.68 (C=O).

(c) *Hydrogenation.* (3RS,6SR)-8-*Benzyl*-3-*methyl*-9-*oxo*-8-*azabicyclo*[4.3.0]*non*-1-*ene*-2-*carboxylic acid* (**53**). A mixture of (1*SR*,2*SR*,3*RS*,6*RS*)-8-benzyl-1,2-dichloro-3-methyl-9-oxo-azabicyclo[4.3.0]non-4-ene-2-carboxylic acid (**41**) and 10% palladium on charcoal (15 mg) in methanol (20 ml) was stirred under hydrogen at 1 atmosphere until hydrogen uptake was complete. The catalyst was filtered off and washed with methanol. The combined filtrate and washings were concentrated under reduced pressure to yield an oil. Purification was achieved by flash column chromatography (eluant, ethyl acetate) to afford (3*RS*,6*SR*)-8-benzyl-3-methyl-9-oxo-8-azabicyclo[4.3.0]non-1-ene-2-carboxylic acid (**53**) (0.07 g, 43%) as an oil, $\nu_{max.}$($CHCl_3$) 2 700—2 100, 1 710, 1 620, and 1 600 cm^{-1}; δ_H(360 MHz) 7.4—7.2 (5 H, complex, Ph), 4.66 (1 H, d, *J* 14.5, C*H*HPh), 4.50 (1 H, d, *J* 14.5 Hz, CH*H*Ph), 3.53 (1 H, dd, *J* 9.0 and 9.0 Hz, 7-H), 3.09 (1 H, dd, *J* 9.0 and 8.5 Hz, 7-H), 3.08 (1 H, m, 3-H), 2.92 (1 H, m, 6-H), 1.88—1.48 (4 H, complex, 4- and 5-H_2), and 1.18 (3 H, d, *J* 7.0 Hz, Me); δ_C 20.60 (CH_2), 22.26 (Me), 29.17 (CH_2), 30.97, 38.24 (CH), 48.03, 51.05 (CH_2), 128.34,

128.45, 129.05 (=CH), 134.62, 138.84, 141.93 (C), 165.19 and 168.69 (C=O).

The following compounds were produced by the same procedure.

Methyl 8-benzyl-9-oxo-8-azabicyclo[4.3.0]*non-1-ene-2-carboxylate* (**54**) as an oil in 28% yield and (1RS,2SR,6RS)-*methyl 8-benzyl-9-oxo-8-azabicyclo*[4.3.0]*nonane-2-carboxylate* (**55**) as an oil in 26% yield from (1*RS*,2*SR*,6*SR*)-methyl 8-benzyl-1,2-dichloro-9-oxo-8-azabicyclo[4.3.0]non-4-ene-2-carboxylate (**31**).

For compound (**54**) (Found: M^+, 285.1368. $C_{17}H_{19}NO_3$ requires *M*, 285.1366); *m/z* 285 (76.7%), 225 (81.6), and 91 (100); $\nu_{max.}$($CHCl_3$) 1 740 and 1 695 cm^{-1}; δ_H(360 MHz) 7.32—7.22 (5 H, complex, Ph), 4.69 (1 H, d, *J* 15.0 Hz, C*H*HPh), 4.48 (1 H, d, *J* 15.0 Hz, CH*H* Ph), 3.72 (5 H, complex, OMe and 7-H_2), 3.41 (1 H, m, 6-H), 2.25 (2 H, complex), and 2.0—1.7 (4 H, complex); δ_H 19.88, 23.83, 26.07 (CH_2), 37.35 (CH), 45.84 (CH_2), 51.79 (OMe), 52.56 (CH_2), 127.24, 128.28, 128.48 (ArC), 117.49, 152.27 (C), and 170.21 and 173.58 (C=O).

For compound (**55**) (Found: M^+, 287.1563. $C_{17}H_{21}NO_3$ requires *M*, 287.1522); *m/z* 287 (44.8%), 227 (51.7), and 91 (100); $\nu_{max.}$($CHCl_3$) 1 740 and 1 695 cm^{-1}; δ_H(360 MHz) 7.3—7.2 (5 H, complex, Ph), 4.58 (1 H, d, *J* 14.5 Hz, C*H*HPh), 4.20 (1 H, d, *J* 14.5 Hz, CH*H* Ph), 3.75 (3 H, s, OMe), 3.32 (1 H, dd, *J* 9.5 and 5.0 Hz, 7-H_α), 3.21 (1 H, d, *J* 6.0, and 6.0 Hz, 1-H), 2.66 (1 H, d, *J* 9.5 Hz, 7-H_β), 2.50 (1 H, ddd, *J* 12.5, 5.0, and 5.0 Hz, 2-H), 2.29 (1 H, dddd, *J* 12.0, 6.0, 6.0, and 6.0 Hz, 6-H), 1.97 (1 H, br d, *J* 11.0 Hz), 1.71 (1 H, ddd, *J* 13.0, 3.5, and 3.5 Hz), 1.59 (1 H, br d, *J* 13.0 Hz), 1.37 (1 H, dddd, *J* 13.0, 13.0, 13.0, and 3.0 Hz), 1.13 (1 H, ddddd, *J* 13.0, 13.0, 13.0, 3.0, and 3.0 Hz), and 0.94 (1 H, dddd, 13.0, 13.0, 13.0, and 3.5 Hz) (together 3-, 4-, and 5-H_2); δ_C 23.29, 23.95, 27.60 (CH_2), 35.58, 40.57, 44.01 (CH), 46.59, 50.91 (CH_2), 51.36 (OMe), 127.36, 128.23, 128.44 (ArC), 136.40 (C), and 172.57 and 173.90 (C=O).

(1*RS*,4*SR*)-8-Benzyl-5-chloro-4-methyl-8-azabicyclo[4.3.0]-non-5-en-7-one (**56**) as a pale yellow oil in 48% yield from (1*RS*,4*SR*)-8-benzyl-5-chloro-4-methyl-8-azabicyclo[4.3.0]-nona-2,5-dien-7-one (**42**), $\nu_{max.}$($CHCl_3$) 1 705 and 1 605 cm^{-1}; δ_H(360 MHz) 7.4—7.2 (5 H, complex, Ph), 4.66 (1 H, d, *J* 14.5 Hz, C*H*HPh), 4.32 (1 H, d, *J* 14.5 Hz, CH*H* Ph), 3.31 (1 H, m, 9-H), 2.83 (2 H, complex, 1- and 9-H), 2.53 (1 H, m, 4-H), 1.89—1.72 (3 H, complex, 3-H_5 or 2- and 3-H_2), 1.36 (1 H, m, 2- or 3-H), and 1.25 (3 H, d, *J* 7.0 Hz, Me); δ_C 19.95 (Me), 21.97, 30.49 (CH_2), 37.03, 38.59 (CH), 46.93, 50.06 (CH_2), 127.63, 128.35, 128.73 (ArC), 133.68, 136.65, 138.72 (C), and 165.82 (C=O).

8-Benzyl-5-chloro-8-azabicyclo[4.3.0]non-5-en-7-one (**57**) as a pale yellow oil in 60% yield from 8-benzyl-5-chloro-8-azabicyclo[4.3.0]nona-3,5-dien-7-one (**44**) (Found: M^+, 261.0917. $C_{15}H_{16}{}^{35}ClNO$ requires *M*, 261.0200); *m/z* 261 (39.4%), 142 (30.3), and 91 (100); $\nu_{max.}$($CHCl_3$) 1 690 and 1 605 cm^{-1}; δ_H(360 MHz) 7.3—7.2 (5 H, complex, Ph), 4.61 (1 H, d, *J* 14.5, C*H*HPh), 4.36 (1 H, d, *J* 14.5 Hz, CH*H* Ph), 3.32 (1 H, m, 9-H), 2.84 (2 H, complex, 1- and 9-H), 2.45 (2 H, complex, CH_2), 1.95 (2 H, complex, CH_2), 1.65 (1 H, m, C*H*H), and 1.21 (1 H, m, CH*H*) (together 2-, 3-, and 4-H_2); δ_C 23.03, 26.05, 34.14 (CH_2), 37.38 (CH), 46.66, 50.02 (CH_2), 116.02 (C), 127.51, 128.22, 128.61 (ArC), 133.49, 136.44 (C), and 165.61 (C=O).

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