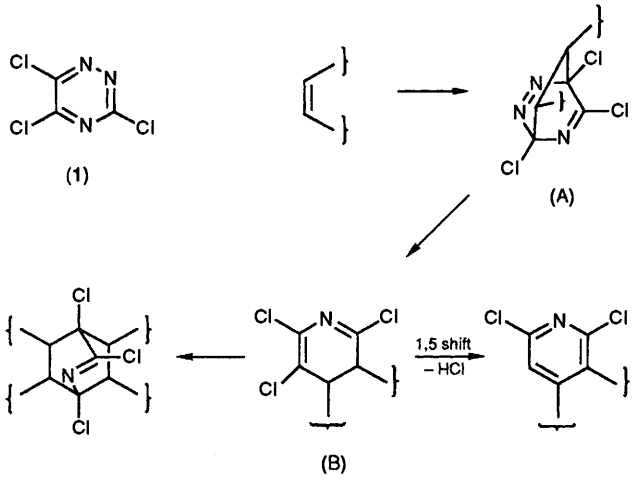
Novel Cage Compounds from Inter- and Intra-Molecular Diels–Alder Reactions of Heteroaromatic Azadienes and Methyl Coumalate with Cyclo-octa-1,5-diene

Ivan Lantos, Peter W. Sheldrake,* and Andrew S. Wells*
Department of Synthetic Chemistry, Smith Kline and French Research Limited, Old Powder Mills, Nr. Leigh, Tonbridge, Kent, TN11 9AN

1,2,4-Triazines, pyridazines, and α-pyrones activated with electron-withdrawing groups were found to react with cyclo-octa-1,5-diene by intermolecular Diels–Alder addition followed by extrusion of nitrogen or carbon dioxide; the resulting 2-aza-1,3-dienes or 1,3-dienes then undergo intramolecular ring-closure reactions to produce novel cage compounds.

Of the various classes of heteroaromatic compounds that act as azadiene fragments in inverse-electron-demand Diels–Alder reactions, the 1,2,4-triazines are probably one of the most intensively investigated.[1–3] Two reactions have been reported to occur between 3,5,6-trichloro-1,2,4-triazine (**1**)[4] and cyclic alkene dienophiles (Scheme 1).[5]



Scheme 1.

The dienophile adds in a [4 + 2]cycloaddition across C-3/C-6 to form the intermediate (A); extrusion of nitrogen produces the 3,4-dihydropyridine (B) which can aromatise *via* a 1,5-sigmatropic proton shift and loss of hydrogen chloride. In some cases intermediate (B) reacts with excess of dienophile in a second [4 + 2]cycloaddition to give polycyclic 2:1 adducts. Several other 1,2,4-triazines have also been reported to form similar 2:1 adducts.[6,7] Our investigations into the Diels–Alder reactions of compound (**1**) showed that the formation of 2:1 adducts is favoured by reactive dienophiles such as cyclic vinyl ethers, and the aromatisation process favoured by simple hydrocarbon dienophiles such as oct-1-ene.[8] It occurred to us that the aromatisation process might be intercepted by a more readily occurring intramolecular Diels–Alder reaction from a strategically placed second olefin moiety. Thus a judiciously chosen diene should react with compound (**1**) by sequential intermolecular addition followed by loss of nitrogen and intramolecular Diels–Alder ring closure giving rise to novel cage compounds.[9] Indeed, such reactions have been reported between sydnones and cyclo-octa-1,5-diene (COD).[10] In this paper we report our results from an investigation into the Diels–Alder reactions between 1,2,4-triazines and related compounds and COD.

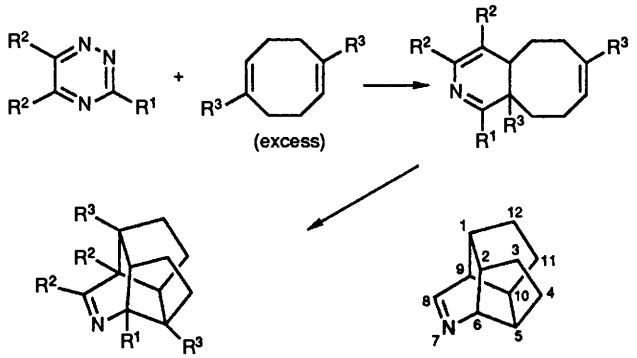
Results and Discussion

(i) 1,2,4-*Triazenes.*—We have already reported in a preliminary communication the reaction between 3,5,6-trichloro-1,2,4-triazine (**1**) and COD to give the novel cage compound 6,8,9-trichloro-7-azatetracyclo[7.3.0.0.^{2,6}0^{5,10}]-dodec-7-ene† (**2**) whose formation is shown in Scheme 2.[11] The compound was synthesized by reaction of the triazine (**1**) with COD (10 mol equiv.) in refluxing xylene. When the reagents were present in a 1:1 stoicheiometry no reaction was detected. Evidently the initial intermolecular addition is favoured by an excess of dienophile, but obviously the intramolecular ring closure is more favourable than the intermolecular addition of a second molecule of COD to the dihydropyridine intermediate. Additional substitution on the cage structure can be introduced using a substituted COD. Hence compound (**3**) was synthesized in 46% yield from the reaction of substrate (**1**) with 1,5-dimethylcyclo-octa-1,5-diene. The linear dienophile, octa-1,7-diene, failed to give an intramolecular reaction: in this case aromatisation occurred producing 2,6-dichloro-3-(hex-5-enyl)-and 2,6-dichloro-4-(hex-5-enyl)pyridine by a mechanism similar to that shown in Scheme 1.

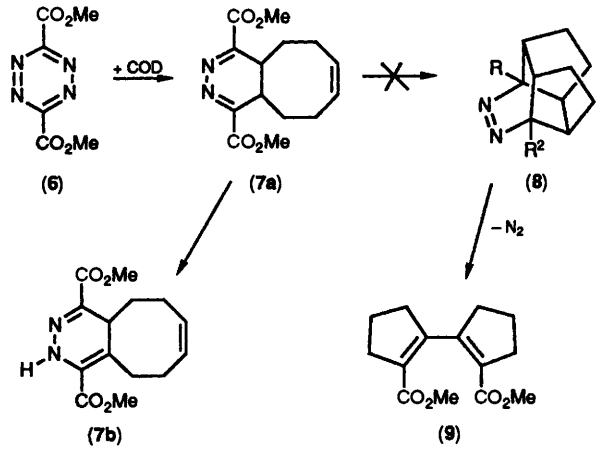
Several other triazines were examined to determine the generality of successive inter- and intra-molecular Diels–Alder reactions. We have reported that both 3-ethoxycarbonyl and 3-methylsulphonyl-1,2,4-triazine reacted with excess of COD at temperatures above 90 °C to give the cage compounds (**4**) and (**5**) in 66 and 44% yield respectively (Scheme 2).[11] However, 3-methyl- and 3-methylthio-1,2,4-triazine failed to react, showing that the triazine nucleus has to be activated with electron-withdrawing substituents to undergo the initial intermolecular cycloaddition with COD. Attempts to replace the methylene groups in compounds (**2**) and (**4**) by ethylene units by reaction of the triazines with cyclo-octa-1,3,5,7-tetraene at high temperatures failed.

An interesting observation was made concerning the hydrolysis of the imidoyl halide cage compounds (**2**) and (**3**). Despite the expected reactivity of imidoyl chlorides to hydrolysis, cage compound (**2**) was very stable towards basic media, *e.g.* refluxing xylene–aqueous NaOH–Bu$^n_4$NCl, and refluxing tetrahydrofuran (THF)–aqueous KOH. This unusual stability towards base hydrolysis has been reported for several other imidoyl halides with similar geometry about the double bond.[5,12,13] In contrast to their stability towards aqueous bases, both compounds (**2**) and (**3**) were very unstable in contact with the atmosphere, degassing HCl, and eventually forming the

† Non-systematic name.



Scheme 2.



Scheme 3.

corresponding lactams. An IR examination of aged samples of compound (**2**) showed absorption bonds of 1 625 cm^{-1} from (**2**), 1 710 cm^{-1} from the lactam of (**2**), and a third species with 1 645 cm^{-1}. The increase of 20 cm^{-1} for the C=N bond stretch wavenumber of compound (**2**) is in accord with the formation of the HCl salt of the imidoyl halide[14] and we expected that this was the species undergoing hydrolysis. This hypothesis was confirmed by the readily occurring hydrolysis of compound (**2**) under mild conditions by aqueous acetone containing HCl at room temperature. The behaviour of compounds (**2**) and (**3**) towards water can be explained by the mechanism of hydrolysis of imidoyl halides. The preferred S_N1-type mechanism involving a nitrilium salt[15] is ruled out by the geometric constraints about the C=N bond in the cage compounds. Similar reasons have been invoked to explain the stability of aza-aldrin to bases and certain nucleophiles.[13] In acidic solution, an alternative addition–elimination mechanism on the protonated imine has been postulated which avoids the formation of nitrilium intermediates.[16]

(ii) *Tetrazines.*—In principle, other heteroaromatic azadienes that can undergo inverse-electron-demand Diels–Alder reactions and extrude nitrogen to reform a diene system could also form similar cage compounds to those produced in the reaction of 1,2,4-triazines with COD. Hence, as a logical extension of the reaction shown in Scheme 2, we examined several other azadiene systems. 3,6-Bis(methoxycarbonyl)-1,2,4,5-tetrazine[17] (**6**) is known to be a highly reactive azadiene[1–3] and we thought that reaction with COD would produce the 4,5-dihydropyridazine (**7a**) after intermolecular cycloaddition and extrusion of nitrogen (Scheme 3). We expected the final product to be the azacage compound (**8**), or the bicyclopentene (**9**). However, the sole product isolated from the reaction of compound (**6**) with COD was the 1,4-dihydropyridazine (**7b**) arising from tautomerisation of compound (**7a**). The conversion of 4,5-dihydropyridazines into 1,4-dihydropyridazines is a common rearrangement, following the Diels–Alder reaction of 1,2,4,5-tetrazines and alkenes.[18–20] The loss of conjugation of the azadiene double bonds, of course, precludes any further intramolecular Diels–Alder reaction. It was possible to oxidise compound (**7b**) to the pyridazine using activated hydroquinones, but no further Diels–Alder reactions were attempted since the product would be a highly strained bridgehead alkene.

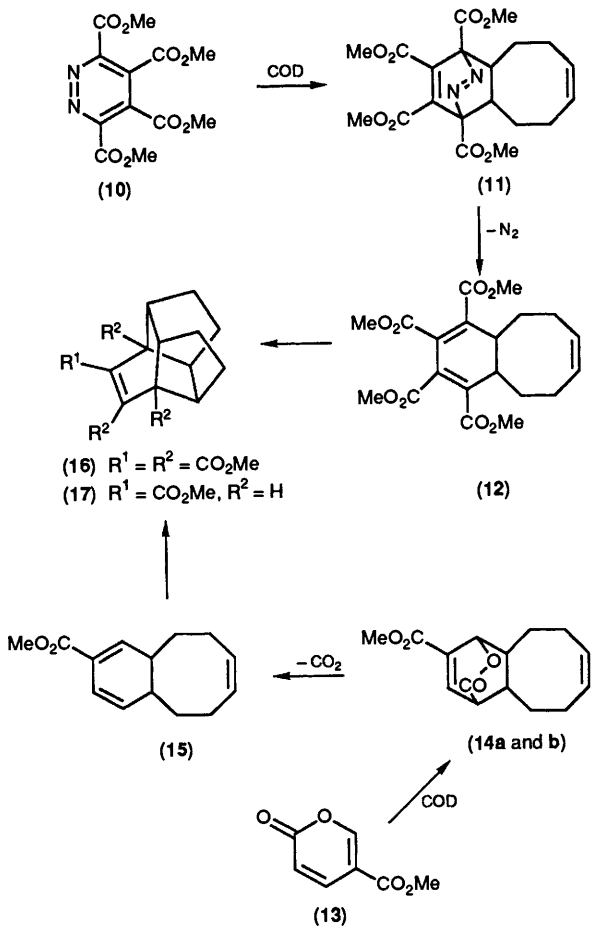
(iii) *Pyridazines.*—The similarity of the types of Diels–Alder reactions undergone by both 1,2,4-triazines and pyridazines suggested to us that pyridazines might be used to synthesize compounds similar to (**2**)–(**5**) but with all-carbon skeletons. Unfortunately, pyridazines proved to be much less reactive towards COD than did triazines. 3,6-Dichloro-, 3,6-bis(methoxycarbonyl)-, 4-hexyl-3,6-bis(methoxycarbonyl)- and 3,6-bis(methoxycarbonyl)-4-phenyl-pyridazine all failed to react with neat COD at 150 °C and were recovered unchanged. 3,6-Dichloro- and 3,6-bis(methoxycarbonyl)-4-phenyl-pyridazine even failed to react with COD at 215 °C in an autoclave. We finally succeeded by using the highly activated 3,4,5,6-tetrabis(methoxycarbonyl)pyridazine[21] (**10**) which gave the all-carbon skeleton cage compound (**16**) albeit in a modest yield of 19%. The formation of compound (**16**) is shown in Scheme 4. As with triazines, the initial Diels–Alder product (**11**) can extrude nitrogen to give the 1,3-diene (**12**), from which the product (**16**) arises *via* intramolecular ring closure.

(iv) *α-Pyrones.*—As an extension of the method, we decided to attempt a synthesis of the all-carbon skeleton of the cage compounds reported here using a precursor without a heteroatom in the 1,3-diene system. α-Pyrones have been reported to undergo intermolecular Diels–Alder reactions and extrude carbon dioxide to regenerate the 1,3-diene.[22–24] Methyl coumalate (**13**) reacted with neat COD at 150 °C to give the expected cage compound (**17**) in 56% yield (Scheme 4). In this reaction, the initial Diels–Alder products (the tricyclic lactones (**14a** and **b**) could be detected in the reaction mixture and isolated by column chromatography. The structures of intermediates (**14a** and **b**) were confirmed spectroscopically, and chemically by the thermal conversion of isolated (**14a** and **b**) into (**17**) in refluxing xylene. The 1,3-diene intermediate (**15**) could not be detected, showing that the intramolecular cycloaddition is much faster than the CO_2 extrusion.

Conclusions.—In conclusion, we have shown that suitably activated 1,2,4-triazines, pyridazines, and α-pyrones can be utilised in the synthesis of tetracyclo[7.3.0.0.^{2,6}0^{5,10}]-dodec-7-ene cage compounds in simple 'one-pot' reactions involving sequential intermolecular Diels–Alder addition, retro-Diels–Alder loss of N_2/CO_2, and intramolecular Diels–Alder ring closure.

Experimental

General.—Starting triazines,[4] pyridazines,[20] and tetrazine[16] were prepared by literature methods. Flash chromatography was performed using 230–400 mesh silica gel. Light petroleum refers to that fraction of 60–80 °C boiling range. M.p.s were



Scheme 4.

determined on a Buchi 510 melting point apparatus and are uncorrected. IR spectra were obtained using a Perkin-Elmer 298 spectrometer, and NMR spectra were recorded on a JEOL GX 270 spectrometer (^1H at 270 MHz, ^{13}C at 67.8 MHz) for solutions in $CDCl_3$ (unless otherwise stated), with tetramethylsilane as internal standard.^{13}C Resonances were assigned using GASPE pulse sequences. Where assignments to specific nuclei have been made the numbering is as shown in Scheme 2. Mass spectra and C, H, N analysis were run by the Physical Organic Chemistry Department, SKF, The Frythe, Welwyn.

6,8,9-*Trichloro*-7-*azatetracyclo*[7.3.0.0.^{2,6}0^{5,10}]*dodec*-7-*ene** (**2**).—3,5,6-Trichlorotriazine (**1**) (1.0 g, 5.4 mmol) was dissolved in anhydrous xylene (10 ml) and COD (6.41 g, 0.059 mol) was added. After the mixture had been refluxed for 3 h, the excess of COD and xylene were removed by distillation under reduced pressure and the residue was treated with hexane (50 ml). After the mixture had been cooled to −10 °C crystallisation occurred to give the *title compound* (**2**) (2.74 g, 65%) as a white crystalline solid, m.p. 120 °C (after recrystallisation from hexane–diethyl ether) (Found: C, 49.9; H, 4.7; N, 5.3%; M^+, 263.000. $C_{11}H_{12}Cl_3N$ requires C, 49.9; H, 4.6; N, 5.3%; *M*, 263.004); $\nu_{max}(CCl_4)$ 1 625 cm^{-1} (N=C); δ_H 2.00 (2 H, m), 2.10 (6 H, m), and 2.35 (4 H, m); δ_C 24.7 and 25.3 (C-3 and -12, -4 and -11), 49.7 and 50.0 (C-1 and -2, and -5 and -10), 84.0 (C-9), 96.1 (C-6), and 159.2 (C-7).

Acid Hydrolysis of Compound (**2**).—Compound (**2**) (0.55 g, 2 mmol) was dissolved in acetone–water (12 ml; 8:2 v/v) and conc. HCl was added (0.25 ml). After being stirred for 17 h the reaction mixture was diluted with water (20 ml) and extracted with CH_2Cl_2 (2 × 20 ml). The combined organic layers were washed with water (20 ml), dried (Na_2SO_4), and the solvent was evaporated off to leave the *lactam of compound* (**2**) (0.45 g, 92%) as a white powder, m.p. 215 °C (from CH_2Cl_2–hexane) (Found: C, 53.1; H, 5.4; N, 5.6%; M^+, 245.041. $C_{11}H_{13}Cl_2NO$ requires C, 53.6; H, 5.3; N, 5.7%; *M*, 245.037); $\nu_{max}(CDCl_3)$ 1 710 (CO), 3 090, and 3 190 cm^{-1} (NH); δ_H 1.90 (7 H, m), 2.10 (1 H, m), 2.28 (2 H, m), 2.50 (2 H, m), and 9.65 (1 H, br s, NH); δ_C[$(CD_3)_2SO$] 22.1 and 23.9 (C-3 and -4, and -11 and -12), 46.9 and 50.00 (C-1 and -2, and -10 and -5), 75.9 (C-9), 82.8 (C-6), and 165.6 (C-8).

6,8,9-*Trichloro*-1,5-*dimethyl*-7-*azatetracyclo*[7.3.0.0.^{2,6}0^{5,10}]-*dodec*-7-*ene** (**3**).—3,5,6-Trichlorotriazine (**1**) (1.5 g, 8.1 mmol) and 1,5-dimethylcyclo-octa-1,5-diene (20 ml) were refluxed for 2 h. After cooling, the reaction mixture was applied to a column and excess of dienophile was eluted with hexane. The product was then eluted with hexane–ethyl acetate (85:15 v/v) and was recrystallised from light petroleum at −10 °C to give the title compound (**3**) (1.10 g, 46%) as a white crystalline solid, m.p. 147–152 °C; $\nu_{max}(CCl_4)$ 1 620 cm^{-1} (N=C); δ_H 1.05 (6 H, Me) and 2.00 (10 H, m). The compound was further analysed after hydrolysis to the lactam.

Lactam of Compound (**3**).—Compound (**3**) (0.91 g, 3 mmol) was finely ground and left exposed to the atmosphere for 36 h. Chromatography with CH_2Cl_2–MeOH (95:5 v/v) as the eluant gave the *lactam of compound* (**3**) (0.75 g, 91%) as white crystals, m.p. 208–218 °C (Found: C, 56.5; H, 6.3; N, 5.1%; M^+, 273.067. $C_{13}H_{17}Cl_2NO$ requires C, 56.9; H, 6.3; N, 5.1%; *M*, 273.068); $\nu_{max}(CCl_4)$ 1 700 (C=O), 3 050, and 3 150 cm^{-1} (NH); δ_H 1.10 (3 H, s, Me), 1.15 (3 H, s, Me), 1.70 (2 H, m), 1.95 (6 H, m), 2.15 (2 H, m), and 7.43 (1 H, br s, NH); δ_C 21.3 (Me), 22.8 (Me), 22.9, 26.1, 31.1, and 32.5 (C-3, -4, -11, and -12), 52.5 and 54.2 (C-1 and -5), 56.1 and 56.7 (C-2 and -10), 81.7 (C-9), 87.2 (C-6), and 166.9 (C-8).

Reaction of 3,5,6-*Trichlorotriazine* (**1**) *with Octa*-1,7-*diene*.—3,5,6-Trichlorotriazine (**1**) (1.0 g, 5.4 mmol) was refluxed with octa-1,7-diene (20 ml) for 3 h. After the mixture had cooled, octa-1,7-diene was removed under reduced pressure and the residue was chromatographed with light petroleum–ethyl acetate (9:1 v/v) to give equal amounts of 2,6-*dichloro*-3-(*hex*-5-*enyl*)*pyridine* and 2,6-*dichloro*-4-(*hex*-5-*enyl*)*pyridine* (0.75 g, 60%) as a pale yellow oil (Found: C, 56.9; H, 5.6; N, 5.8%; M^+, 229.046. $C_{11}H_{13}Cl_2N$ requires C, 57.4; H, 5.7; N, 6.1%; *M*, 229.049); ν_{max}(neat) 1 590 cm^{-1} (N=C); δ_H 1.48 (2 H, m, $CH_2C_3H_5$) 1.66 (2 H, m, $CH_2C_4H_7$), 2.13 (2 H, m, $CH_2C_2H_3$), 2.61 and 2.70 (2 H, t, $CH_2C_5H_9$), 5.00 (2 H, m, CH=CH_2), 5.78 (1 H, m, CH=CH_2), 7.10 (1 H, s, pyridine 3-H), 7.10 (0.5 H, d, pyridine 5-H), and 7.53 (0.5 H, d, pyridine 4-H).

Ethyl 7-*Azatetracyclo*[7.3.0.0.^{2,6}0^{5,10}]*dodec*-7-*ene*-6-*carboxylate** (**4**).—Ethyl-1,2,4-triazine-3-carboxylate (1.0 g, 6.5 mmol) was refluxed in anhydrous toluene (5 ml) containing COD (7.02 g, 0.065 mol) for 3 h. Toluene and excess of COD were removed by distillation and the residue was chromatographed with hexane–ethyl acetate (1:1 v/v) as the eluant to give the *title compound* (**4**) (1.04 g, 66%) as a pale yellow oil (Found: C, 71.5; H, 8.3; N, 5.9%; M^+, 233.141. $C_{14}H_{19}NO_2$ requires C, 72.1; H, 8.2; N, 6.0%; *M*, 233.142); ν_{max}(neat) 1 735

* Non-systematic name.

(CO) and 1 635 cm^{-1} (N=C); δ_H 1.32 (3 H, t, Me), 1.61 (4 H, m), 1.86 (2 H, m), 1.95 (2 H, m), 2.05 (2 H, m), 2.19 (2 H, m), 2.50 (1 H, dd, 5-H), 4.30 (2 H, q, CH_2Me), and 8.46 (1 H, d, *J* 6 Hz, 8-H); δ_C 14.2 (Me), 23.1 and 25.8 (C-3 and -4, and -11 and -12), 39.2 and 40.5 (C-1 and -10, and -2 and -5), 43.7 (C-9), 55.8 (CH_2Me), 74.7 (C-6), 171.8 (C-8), and 174.2 (CO).

6-Methylsulphonyl-7-azatetracyclo[7.3.0.0.^{2,6}0^{5,10}]*dodec-7-ene** (**5**).—3-Methylsulphonyl-1,2,4-triazine (0.9 g, 5.7 mmol) was refluxed in anhydrous toluene (7 ml) containing COD (7.0 g, 0.065 mol) for 2.5 h. The product was isolated as described for compound (**4**) to give the *title compound* (**5**) (0.6 g, 44%) as an off-white crystalline solid, m.p. 102–106 °C (Found: C, 60.3; H, 7.0; N, 6.0. $C_{12}H_{17}NO_2S$ requires C, 60.3; H, 7.1; N, 5.9%); $\nu_{max}(CCl_4)$ 1 650 (N=C), and 1 310 and 1 135 cm^{-1} (SO_2); δ_H 1.65 (2 H, m), 1.94 (2 H, m), 2.06 (2 H, m), 2.15 (2 H, m), 2.25 (2 H, m), 2.50 (2 H, m), 2.55 (1 H, m, 5-H), 2.78 (1 H, d, d), 3.15 (3 H, s, Me), and 8.47 (1 H, d, *J* 6 Hz, 8-H); δ_C 23.7 and 25.3 (C-3 and -4, and -11 and -12), 38.4 (C-9), 41.1 and 41.3 (C-1 and -10, and -2 and -5), 44.2 (Me), 93.2 (C-6), and 172.1 (C-8).

Reaction of Dimethyl 1,2,4,5-*Tetrazine*-3,6-*dicarboxylate with COD: Formation of Compound* (**7b**).—Dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (2.0 g, 0.01 mol) was refluxed in a mixture of anhydrous toluene (10 ml) and COD (15 ml) for 1 h. After cooling, the reaction mixture was applied to a column and toluene and excess of COD were eluted with hexane. The product was eluted with hexane–ethyl acetate (1:1 v/v) to give *compound* (**7b**) (2.32 g, 85%) as a crystalline yellow solid, m.p. 102–103 °C (Found: C, 60.2; H, 6.5; N, 10.0%; M^+, 278. $C_{14}H_{18}N_2O_4$ requires C, 60.4; H, 6.5; N, 10.1%; *M*, 278); $\nu_{max}(CCl_4)$ 1 735 (CO), 1 710 (CO), 1 635 (C=C–CO), and 1 590 cm^{-1} (N=C); δ_H 1.33 (2 H, m), 1.75 (1 H, m), 2.03 (2 H, m), 2.40 (2 H, m), 3.55 (1 H, m), 3.68 (1 H, m), 3.90 (3 H, s, Me), 3.92 (3 H, s, Me), 5.75 (2 H, m, HC=CH), and 8.74 (1 H, br s, NH).

Tetramethyl Tetracyclo[7.3.0.0.^{2,6}0^{5,10}]*dodec-7-ene*-6,7,8,9-*tetracarboxylate** (**16**).—Tetramethyl pyridazine 3,4,5,6-tetracarboxylate (0.4 g, 1.3 mmol) was refluxed in a mixture of anhydrous xylene (5 ml) and COD (15 g, 0.14 mol) for 20.5 h. After cooling, the reaction mixture was chromatographed with light petroleum to elute xylene and COD, then with light petroleum–ethyl acetate (7:3 v/v) to elute the product. Recrystallisation from light petroleum–acetone gave the *title compound* (**16**) (0.095 g, 19%) as a white crystalline solid, m.p. 187 °C (Found: C, 60.9; H, 6.1%; M^+, 392. $C_{20}H_{24}O_8$ requires C, 61.2; H, 6.1%; *M*, 392); $\nu_{max}(CCl_4)$ 1 755 (C=O), 1.735 (C=O), and 1 650 cm^{-1} (C=C); δ_H 1.73 (4 H, d, 1.90 (4 H, d), 2.44 (4 H, s), 3.72 (6 H, s, Me), and 3.76 (6 H, s, Me); δ_C 24.4 (C-3, -4, -11, and -12), 43.9 (C-1, -2, -5, and -10), 52.2 (Me), 52.4 (Me), 58.3 (C-6 and -9), 137.8 (C-7 and -8), 165.5 (*C*OC=C), and 173.1 (CO).

Methyl Tetracyclo[7.3.0.0.^{2,6}0^{5,10}]*dodec-7-ene-7-carboxylate** (**17**).—Methyl coumalate (**13**) (3.0 g, 0.019 mol) was refluxed in COD (30 ml) for 3.5 h. After removal of excess of COD by distillation, the residue was applied to a column and washed with hexane then eluted with hexane–ethyl acetate (7:3 v/v). Compound (**17**) was eluted first, followed by lactones (**14a**) and (**14b**). Compound (**17**) was further purified by rechromatography with diethyl ether–hexane (3:7 v/v) as the eluant to give the *title compound* (**17**) (2.33 g, 56%) as a pale yellow oil (Found: C, 76.9; H, 8.3%; M^+, 218. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%; *M*, 218); ν_{max}(neat) 1 710 (C=O) and 1 640 cm^{-1} (C=C); δ_H 1.54 (4 H, m), 1.79 (8 H, m), 2.40 (1 H, m), 2.88 (1 H, m), 3.88 (3 H, s, Me), and 7.35 (1 H, d, *J* 12 Hz, 8-H); δ_C 25.5 and 26.0 (C-3 and -4, and -11 and -12), 40.0 and 40.5 (C-1 and -10, -2 and -5), 41.8 (C-9), 44.0 (C-6), 51.5 (Me), 134.5 (C-7), 142.0 (C-8), and 165.1 (C=O).

Compounds (**14a**) and (**14b**) were further purified by rechromatography with diethyl ether–hexane (3:7 v/v) to give a mixture (0.65 g, 13%) as a viscous oil [Found: M^+, 262 (FAB-MS). $C_{15}H_{18}O_4$ requires *M*, 262]; ν_{max}(neat) 1 760 (lactone C=O), 1 720 (C=O), and 1 640 cm^{-1} (C=C); δ_H 2.00 (6 H, m), 2.42 (4 H, m), 3.35 and 3.52 (1 H, d), 3.78 and 3.81 (3 H, s, Me), 5.40 (1 H, m), 5.73 (2 H, m, HCCH), and 7.35 (1 H, m, HC=CCO). Integral ratios indicate a 60:40 mixture of isomers.

Conversion of Isolated Intermediates (**14a**) *and* (**14b**) *into Compound* (**17**).—The tricyclic lactones (0.40 g, 1.5 mmol) were dissolved in anhydrous xylene and the solution was refluxed for 16 h. The reaction mixture was cooled and applied to a chromatography column. Xylene was eluted with hexane, then the product was eluted with hexane–ethyl acetate (8:2 v/v) to give compound (**17**) (0.35 g, 84%). The product was identical with the product isolated from the previous section.

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