

Generation and Diels–Alder Reactions of 3-Acyl-3-pyrroline-2,5-diones

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A series of 3-acyl-3-pyrroline-2,5-diones (**13**)–(**17**) have been generated in solution by oxidative elimination from the corresponding 3-acyl-3-phenylselenopyrrolidine-2,5-diones (**8**)–(**12**), and trapped by the conjugated dienes, *trans,trans*-hexa-2,4-diene and cyclopentadiene, to give modest to good yields of the Diels–Alder adducts (**18**)–(**27**). The imido ring dominated the *endo*–*exo* selectivity.

The use of the Diels–Alder reaction as a synthetic method is still being developed. Recently some Diels–Alder reactions of the methoxycarbonylmaleic anhydride (**1**) were described.¹ We here report the generation in solution of a series of related dienophiles, namely 3-acyl-3-pyrroline-2,5-diones (**13**)–(**17**), which were studied because of their possible use in a proposed cytochalasan synthesis,² and which were found to undergo rapid Diels–Alder reactions with simple conjugated dienes.

Results and Discussion

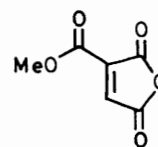
1-Methylpyrrolidine-2,5-dione (**2**) was acylated at the 3-position, following the published procedure, using an ester and sodium hydride in tetrahydrofuran, in the presence of a catalytic amount of an alcohol, either methanol or ethanol.³ The 3-acylpyrrolidine-2,5-diones (**3**)–(**7**) so prepared were found to exist predominantly in their keto-forms; enolisation occurred to a small extent (*ca.* 10%), as shown by ¹H n.m.r. spectroscopy. Benzeneselenenylation was then achieved by treatment of the 3-acylpyrrolidine-2,5-diones with sodium hydride and benzeneselenenyl chloride to give the corresponding 3-phenylseleno products (**8**)–(**12**).⁴ These selenides were oxidised using two equivalents of *m*-chloroperoxybenzoic acid in dichloromethane at –15 °C. After 15 min, excess of pyridine was added, followed by an excess of either cyclopentadiene or *trans,trans*-hexa-2,4-diene. The Diels–Alder adducts (**18**)–(**27**) were then isolated after the mixture had been stirred for 1–2 h at room temperature. The products obtained, together with their yields, are given in the Scheme.

The Diels–Alder adducts were identified on the basis of their spectroscopic data. For each of the cyclopentadiene reactions, the high field (300 MHz) ¹H n.m.r. spectrum of the crude product mixture showed the presence of two products in the ratio *ca.* 85:15. In all cases the major product was isolated pure, and identified as the adduct with the stereochemistry shown in

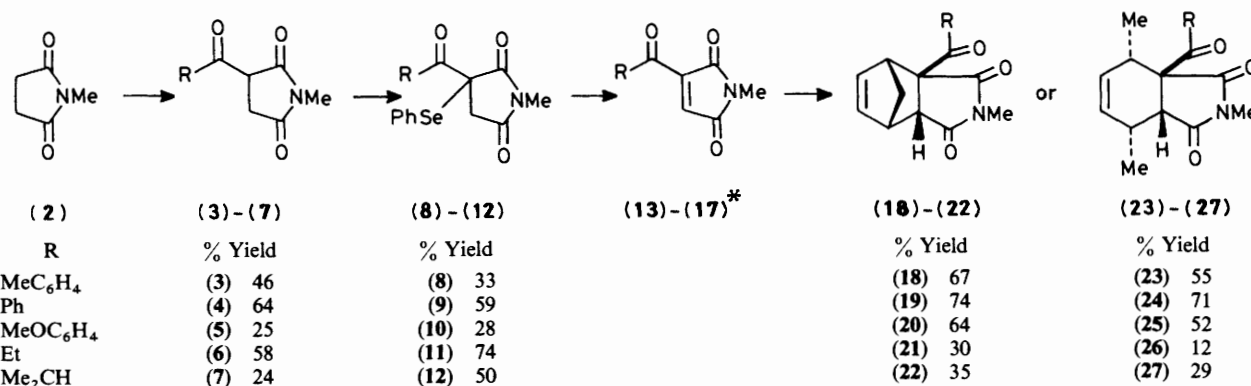
Figure 1, *i.e.* with the imido ring in the *endo* position. This stereochemistry was established by spin-decoupling experiments which showed the presence of coupling, *J ca.* 4.6 Hz, between the *exo* proton, 6-H, and the bridgehead proton, 7-H. This coupling, together with the absence of long-range coupling between 6-H and the *anti*-methylene bridge proton, 10'-H, established that the stereochemistry is as shown.⁵ The minor product from each of the cyclopentadiene reactions was assumed to be the Diels–Alder adduct with the imido ring *exo*. The ¹H n.m.r. data obtained were consistent with this, but it was not possible to isolate pure samples of these minor products for proper characterisation.

For the *trans,trans*-hexa-2,4-diene adducts (**23**)–(**27**), only a single Diels–Alder adduct was detected in each case, identified as the adduct with the imido ring *endo* as shown in Figure 2. This stereochemical assignment was made by analogy with the cyclopentadiene adducts discussed above, and is consistent with the H(5)–H(6) coupling constants, *J* 5–5.7 Hz, which are in the range expected for such systems.^{2,6} These adducts would appear to adopt the boat conformation shown. Thus, the vinylic protons give rise to a symmetric AB system of triplets in their ¹H n.m.r. spectra.

These observations show that 3-acylpyrroline-2,5-diones can be generated and trapped as Diels–Alder adducts. Preliminary attempts were made to isolate these intermediate dienophiles but were unsuccessful, only polymeric material being obtained.



(1)



Scheme. * The pyrrolidiones (**13**)–(**17**) were not isolated.

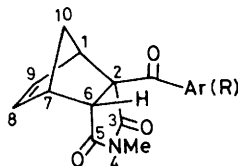


Figure 1.

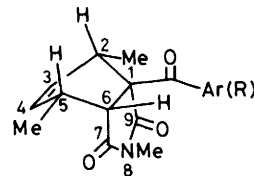


Figure 2.

The yields of the Diels–Alder adducts from the 3-acylpyrrolidine-2,5-diones (**13**)–(**15**) were quite reasonable, being in the range 50–75%. However, lower yields were obtained from the aliphatic analogues (**16**) and (**17**), possibly because of competing polymerisation initiated by enolisation. The speed of the Diels–Alder reactions of the acylpyrrolidine-2,5-diones, all of which were complete in less than 2 h at room temperature, is consistent with the electron deficient nature of the double bond in these systems.⁷ Since there exists considerable synthetic methodology based on reactions of imides, these Diels–Alder reactions may prove to be useful in synthesis.

Experimental

I.r. spectra were measured on Perkin-Elmer 257 and 297 spectrophotometers, and ¹H n.m.r. spectra on a Bruker WH-300 spectrometer (300 MHz). M.p.s were determined on a Buchi 510 apparatus, and are uncorrected. Mass spectra were measured on a VG-micromass ZAB-16F spectrometer using either electron impact (E.I.) or chemical ionization (C.I.) modes.

T.l.c. was carried out using Merck aluminium sheets, precoated with silica gel 60F₂₅₄; flash chromatography was on Merck silica gel 60, and short column chromatography used Merck Keisegel 60H.

All solvents were dried and distilled before use. Ether refers to diethyl ether throughout and light petroleum to the fraction with b.p. 40–60 °C. 1-Methylpyrrolidine-2,5-dione (**2**) was prepared by treatment of succinic anhydride with methylamine in aqueous ethanol,⁸ m.p. 64 °C (from isopropyl alcohol) (lit.,⁹ 66–68 °C).

General Procedure for the Acylation of 1-Methylpyrrolidine-2,5-dione (2).—The ester (2 mol equiv.) and a few drops of methanol (for methyl esters) or ethanol (for ethyl esters), were added to 1-methylpyrrolidine-2,5-dione (**2**) in anhydrous tetrahydrofuran (THF). Sodium hydride (60% dispersion in oil, 2 mol equiv.) was added in small portions, and the heterogeneous mixture heated under reflux for 16–20 h, cooled, and ether and water were added. The aqueous phase was separated, acidified with glacial acetic acid, and extracted into dichloromethane. After being dried (MgSO₄), the organic extract was concentrated under reduced pressure, and the product isolated by crystallisation or distillation. The following compounds were prepared. 1-Methyl-3-(4-methylbenzoyl)pyrrolidine-2,5-dione (**3**) (46%), m.p. 107–109 °C (from methanol) (Found: C, 67.4; H, 5.55; N, 6.05. C₁₃H₁₃NO₃ requires C, 67.5; H, 5.65; N, 6.05%); ν_{\max} (CH₂Cl₂) 3 060 (aromatic CH), 1 780, 1 710, and 1 680 (C=O), and 1 610 cm⁻¹ (aromatic ring); δ_{H} (CDCl₃) 2.45 (3 H, s, aromatic Me), 2.85 (1 H, dd, *J* 18, 9 Hz, 4-H), 3.01 (3 H, s, NMe), 3.39 (1 H, dd, *J* 18, 4 Hz, 4-H), 4.83 (1 H, dd, *J* 9, 4 Hz, 3-H), and 7.33 and 8.00 (each 2 H, m, aromatic H); *m/z* (E.I.) 231 (*M*⁺, 6%) and 119 (*M*⁺ – 112, 100).

3-Benzoyl-1-methylpyrrolidine-2,5-dione (**4**) (64%), m.p. 100–103 °C (from methanol) (Found: C, 66.15; H, 5.15; N, 6.6. C₁₂H₁₁NO₃ requires C, 66.35; H, 5.1; N, 6.45%); ν_{\max} (CH₂Cl₂) 3 060 (aromatic CH), 1 785 and 1 700 (C=O), and 1 600 cm⁻¹ (aromatic ring); δ_{H} (CDCl₃) 2.86 (1 H, dd, *J* 18, 9 Hz, 4-H), 3.00 (3 H, s, NMe), 3.37 (1 H, dd, *J* 18, 4 Hz, 4-H), 4.85 (1 H, dd, *J*

9, 4 Hz, 3-H), 7.58 (3 H, m, aromatic H), and 8.12 (2 H, m, aromatic H); *m/z* (E.I.) 217 (*M*⁺, 7%) and 105 (*M*⁺ – 112, 100).

3-(4-Methoxybenzoyl)-1-methylpyrrolidine-2,5-dione (**5**) (25%), m.p. 119–120.5 °C (from methanol) (Found: C, 63.1; H, 5.3; N, 5.7. C₁₃H₁₃NO₄ requires C, 63.15; H, 5.3; N, 5.65%); ν_{\max} (CH₂Cl₂) 1 780, 1 705, and 1 675 (C=O), and 1 600 cm⁻¹ (aromatic); δ_{H} (CDCl₃) 2.82 (1 H, dd, *J* 18, 9 Hz, 4-H), 2.97 (3 H, s, NMe), 3.37 (1 H, dd, *J* 18, 4 Hz, 4-H), 3.89 (3 H, s, OMe), 4.78 (1 H, dd, *J* 9, 4 Hz, 3-H), and 6.99 and 8.08 (each 2 H, m, aromatic H); *m/z* (E.I.) 247 (*M*⁺, 4%), 152 (*M*⁺ – 95, 61), and 135 (*M*⁺ – 112, 100).

3-(1-Oxopropyl)-1-methylpyrrolidine-2,5-dione (**6**) (58%), b.p. 200–210 °C at 0.9 mmHg (Found: C, 56.65; H, 6.25; N, 8.2. C₈H₁₁NO₃ requires C, 56.8; H, 6.55; N, 8.3%); ν_{\max} (liq. film) 1 780 and 1 710 cm⁻¹ (C=O); δ_{H} (CDCl₃) 1.11 (3 H, t, *J* 7.5 Hz, CH₂CH₃), 2.64 (1 H, dq, *J* 19, 7.5 Hz, HCHCH₃), 2.67 (1 H, dd, *J* 20, 10 Hz, 4-H), 2.97 (3 H, s, NMe), 3.14 (1 H, dq, *J* 19, 7.5 Hz, HCHCH₃), 3.32 (1 H, dd, *J* 20, 5 Hz, 4-H), and 3.95 (1 H, dd, *J* 10, 5 Hz, 3-H); *m/z* (E.I.) 169 (*M*⁺, 9%) 113 (*M*⁺ – 56, 41), and 57 (*M*⁺ – 112, 100).

1-Methyl-3-(2-methyl-1-oxopropyl)pyrrolidine-2,5-dione (**7**) (24%), b.p. 175–180 °C at 0.7 mmHg (Found: C, 58.95; H, 7.3; N, 7.65. C₉H₁₃NO₃ requires C, 59.0; H, 7.15; N, 7.65%); ν_{\max} (liq. film) 1 780 and 1 710 cm⁻¹ (C=O); δ_{H} (CDCl₃) 1.13 and 1.20 (each 3 H, d, *J* 7 Hz, CHMe₂), 2.67 (1 H, dd, *J* 18, 9 Hz, 4-H), 2.96 (3 H, s, NMe), 3.21 (2 H, m, CHMe₂ + 4-H), and 4.13 (1 H, dd, *J* 9, 4 Hz, 3-H); *m/z* (E.I.) 183 (*M*⁺, 8%) and 71 (*M*⁺ – 112, 40).

General Procedure for the Benzeneselenenylation of 3-Acyl-1-methylpyrrolidine-2,5-diones.—The 3-acyl-1-methylpyrrolidine-2,5-dione (1 mol equiv.) was added to a suspension of sodium hydride (1.2 mol equiv., 60% dispersion in oil, washed 3 × with light petroleum) in anhydrous THF at 0 °C, and the mixture allowed to warm to ca. 20 °C and stirred for 30 min. After recooling to 0 °C, benzeneselenenyl chloride (1.1 mol equiv.) in anhydrous THF was added, and the mixture again allowed to warm to ca. 20 °C and stirred for 30 min. After the addition of ether and saturated aq. NaHCO₃ the ethereal phase was separated, dried (MgSO₄), and concentrated under reduced pressure to give the impure products which were crystallised or purified by flash chromatography (eluted with 1:1 light petroleum–ether). The following compounds were so prepared. 1-Methyl-3-(4-methylbenzoyl)-3-phenylselenopyrrolidine-2,5-dione (**8**) (33%), m.p. 152–154 °C (from benzene–methanol); ν_{\max} (CH₂Cl₂) 1 780, 1 710, and 1 670 (C=O), and 1 610 cm⁻¹ (aromatic); δ_{H} (CDCl₃) 2.44 (3 H, s, aromatic Me), 2.78 (3 H, s, NMe), 3.11 and 3.77 (each 1 H, d, *J* 19 Hz, CH₂), 7.4 (7 H, m, aromatic H), and 7.99 (2 H, m, aromatic H); *m/z* (E.I.) 385, 387 (*M*⁺, 0.7%) and 119 (*M*⁺ – 266, 268, 100).

3-Benzoyl-1-methyl-3-phenylselenopyrrolidine-2,5-dione (**9**) (59%), m.p. 152–154 °C (from benzene) (Found: C, 58.3; H, 4.05; N, 3.95. C₁₈H₁₅NO₃Se requires C, 58.1; H, 4.05; N, 3.75%); ν_{\max} (CH₂Cl₂) 3 060 (aromatic CH), 1 780, 1 710, 1 680 (C=O), and 1 595 cm⁻¹ (aromatic ring); δ_{H} (CDCl₃) 2.79 (3 H, s, NMe), 3.11 and 3.78 (each 1 H, d, *J* 19 Hz, CH₂), 7.5 (8 H, m, aromatic H), and 8.10 (2H, m, aromatic H); *m/z* (C.I.) 372, 374 (*M*⁺ + 1, 4%).

3-(4-Methoxybenzoyl)-1-methyl-3-phenylselenopyrrolidine-2,5-dione (10) (28%), m.p. 119–121 °C (from benzene-ether); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 1780, 1710, and 1665 (C=O), and 1600 and 1580 cm^{-1} (aromatic ring); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.78 (3 H, s, NMe), 3.10 and 3.83 (each 1 H, d, J 19 Hz, CH_2), 3.89 (3 H, s, OMe), 6.97 (2 H, m, aromatic H), 7.45 (5 H, m, aromatic H), and 8.17 (2 H, m, aromatic H); m/z (E.I.) 401, 403 (M^+ , 3%), 245 ($M^+ - 156, 158, 53$), 155 and 157 ($M^+ - 246, 48$), and 135 ($M^+ - 266, 268, 100$).

3-(1-Oxopropyl)-1-methyl-3-phenylselenopyrrolidine-2,5-dione (11) (74%), m.p. 62–64 °C (from ether-benzene) (Found: C, 51.55; H, 4.85; N, 4.6. $\text{C}_{14}\text{H}_{15}\text{NO}_3\text{Se}$ requires C, 51.85; H, 4.65; N, 4.3%); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 1780 and 1710 cm^{-1} (C=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.15 (3 H, t, J 7.3 Hz, CH_2CH_3), 2.69 (1 H, d, J 19.5 Hz, 4-H), 2.88 (3 H, s, NMe), 2.96 and 3.34 (each 1 H, dq, J 18.5, 7 Hz, CH_2CH_3), 3.56 (1 H, d, J 19.5 Hz, 4-H), and 7.4 (5 H, m, aromatic H); m/z (E.I.) 325, 323 (M^+ , 6%).

1-Methyl-3-(2-methyl-1-oxopropyl)-3-phenylselenopyrrolidine-2,5-dione (12) (56%), m.p. 64–66 °C (from benzene-light petroleum) (Found: C, 53.5; H, 5.1; N, 4.25. $\text{C}_{15}\text{H}_{17}\text{NO}_3\text{Se}$ requires C, 53.25; H, 5.05; N, 4.15%); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 1780 and 1710 cm^{-1} (C=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.02 and 1.36 (each 3 H, d, J 5 Hz, HCHMe_2), 2.66 (1 H, d, J 20 Hz, 4-H), 2.93 (3 H, s, NMe), 3.49 (1 H, d, J 20 Hz, 4-H), 3.87 (1 H, h, J 5 Hz, HCHMe_2), and 7.43 (5 H, m, aromatic H); m/z 337, 339 (M^+ , 4%).

Generation and Diels-Alder Reactions of 3-Acyl-3-pyrrolidine-2,5-diones (13)–(17).—*m*-Chloroperoxybenzoic acid (2 mol equiv.) was added to the phenylselenopyrrolidine-2,5-dione in anhydrous dichloromethane at -15 °C. After the mixture had been stirred for 10–15 min at -15 °C, pyridine (3.1 mol equiv.) and the diene (10 mol equiv.) were added, and the mixture was allowed to warm to ca. 20 °C and stirred for 1 h (using cyclopentadiene) and for 2 h (using *trans,trans*-hexa-2,4-diene). After the addition of 1M-aqueous NaOH and more CH_2Cl_2 , the organic phase was separated, dried (MgSO_4), and concentrated under reduced pressure. The products were purified by short column chromatography (eluted with light petroleum-ether). The ^1H n.m.r. spectra of the crude products from the cyclopentadiene reactions indicated the presence of two components in each case, ratio ca. 85:15. The major component was isolated pure (see text). The following adducts were characterised. (1RS,2SR,6RS,7SR)-4-Methyl-2-(4-methylbenzoyl)-3,5-dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene (18) (67%), m.p. 127–128 °C (from ether-benzene) (Found: C, 72.85; H, 5.9; N, 4.65. $\text{C}_{18}\text{H}_{17}\text{NO}_3$ requires C, 73.2; H, 5.8; N, 4.75%); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 3020 (aromatic H), 1770, 1705, and 1670 (C=O), and 1610 cm^{-1} (aromatic ring); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.53 (1 H, d, J 9 Hz, 10-H), 1.72 (1 H, dt, J 9, 1.6 Hz, 10-H), 2.42 (3 H, s, aromatic Me), 2.88 (3 H, s, NMe), 3.41 and 3.88 (each 1 H, m, 7-H and 1-H), 4.01 (1 H, d, J 4.7 Hz, 6-H), 6.27 (2 H, m, vinylic H), and 7.32 and 8.06 (each 2 H, m, aromatic H); m/z (E.I.) 295 (M^+ , 2%) and 119 ($M^+ - 176, 100$).

(1RS,2SR,6RS,7SR)-2-Benzoyl-4-methyl-3,5-dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene (19) (74%), m.p. 95–98 °C (from ether) (Found: C, 72.45; H, 5.25; N, 5.05. $\text{C}_{17}\text{H}_{15}\text{NO}_3$ requires C, 72.6; H, 5.35; N, 5.0%); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 3060 (aromatic H), 1775 and 1705 (C=O), and 1600 and 1580 cm^{-1} (aromatic ring); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.53 (1 H, d, J 9 Hz, 10-H), 1.74 (1 H, dt, J 9, 1.6 Hz, 10-H), 2.89 (3 H, s, NMe), 3.42 and 3.88 (each 1 H, m, 7-H and 1-H), 4.05 (1 H, d, J 4.6 Hz, 6-H), 6.29 (2 H, m, vinylic H), 7.55 (3 H, m, aromatic H), and 8.15 (2 H, m, aromatic H); m/z (E.I.) 281 (M^+ , 5%), 216 ($M^+ - 65, 24$), and 105 ($M^+ - 176, 100$).

(1RS,2SR,6RS,7SR)-2-(4-Methoxybenzoyl)-4-methyl-3,5-dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene (20) (64%), m.p. 151–152 °C (from ether-light petroleum) (Found: C, 69.55; H, 5.7; N, 4.3. $\text{C}_{18}\text{H}_{17}\text{NO}_4$ requires C, 69.45; H, 5.5; N, 4.5%);

$\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 1770 and 1700 (C=O), and 1600 cm^{-1} (aromatic); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.54 and 1.70 (each 1 H, d, J 9.2 Hz, CH_2), 2.87 (3 H, s, NMe), 3.41 and 3.87 (each 1 H, m, 7-H and 1-H), 3.89 (3 H, s, OMe), 4.08 (1 H, d, J 4.6 Hz, 6-H), 6.28 (2 H, m, vinylic H), and 6.97 and 8.22 (each 2 H, m, aromatic H); m/z (E.I.) 311 (M^+ , 5%), and 135 ($M^+ - 176, 100$).

(1RS,2SR,6RS,7SR)-2-(1-Oxopropyl)-4-methyl-3,5-dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene (21) (30%), a colourless oil (Found: M^+ , 233.1051. $\text{C}_{13}\text{H}_{15}\text{NO}_3$ requires M , 233.1052); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 1775 and 1700 cm^{-1} (C=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.09 (3 H, t, J 7 Hz, CH_2CH_3), 1.58 (1 H, br d, J 9 Hz, 10-H), 1.70 (1 H, dt, J 9, 1.5 Hz, 10-H), 2.84 (3 H, s, NMe), 2.84 and 2.92 (each 1 H, dq, J 19, 7 Hz, CH_2CH_3), 3.38 and 3.52 (each 1 H, m, 7-H and 1-H), 3.72 (1 H, d, J 4.6 Hz, 6-H), and 6.19 (2 H, m, vinylic H); m/z (E.I.) 233 (M^+ , 14%), 177 ($M^+ - 56, 33$), 168 ($M^+ - 65, 38$), and 66 ($M^+ - 167, 100$).

(1RS,2SR,6RS,7SR)-4-Methyl-2-(2-methyl-1-oxopropyl)-3,5-dioxo-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene (22) (35%), m.p. 63–64 °C (from ether-light petroleum) (Found: C, 67.9; H, 6.75; N, 5.7. $\text{C}_{14}\text{H}_{17}\text{NO}_3$ requires C, 68.0; H, 6.95; N, 5.65%); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 3060 (vinylic CH), and 1775 and 1700 cm^{-1} (C=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.08 and 1.16 (each 3 H, d, J 6.7 Hz, CHMe_2), 1.64 (1 H, br d, J 9 Hz, 10-H), 1.71 (1 H, dt, J 9, 1.5 Hz, 10-H), 2.85 (3 H, s, NMe), 3.40 (1 H, m, 7-H), 3.49 (1 H, h, J 6.7 Hz, CHMe_2), 3.58 (1 H, m, 1-H), 3.71 (1 H, d, J 4.6 Hz, 6-H), and 6.21 (2 H, m, vinylic H); m/z (E.I.) 247 (M^+ , 11%), 177 ($M^+ - 70, 50$), 66 ($M^+ - 181, 84$), and 43 ($M^+ - 244, 100$).

(1SR,2SR,5RS,6SR)-1-(4-Methylbenzoyl)-2,5,8-trimethyl-7,9-dioxo-8-azabicyclo[4.3.0]non-3-ene (23) (55%), m.p. 110–112 °C (from ether-light petroleum) (Found: C, 73.3; H, 6.9; N, 4.65. $\text{C}_{19}\text{H}_{21}\text{NO}_3$ requires C, 73.3; H, 6.8; N, 4.5%); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 3040 (aromatic CH), 1775 and 1705 (C=O), and 1610 cm^{-1} (aromatic ring); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.29 and 1.49 (each 3 H, d, J 7 Hz, 2 \times CHCH_3), 2.39 (3 H, s, aromatic Me), 2.55 (1 H, m, 5-H), 3.02 (3 H, s, NMe), 3.20 (1 H, d, J 5.3 Hz, 6-H), 3.32 (1 H, m, 2-H), 5.68 and 5.73 (each 1 H, dt, J 9, 3 Hz, vinylic H), 7.22 (2 H, m, aromatic H), and 7.53 (2 H, m, aromatic H); m/z (E.I.) 311 (M^+ , 1%), 192 ($M^+ - 119, 100$), 119 ($M^+ - 192, 100$), and 91 ($M^+ - 220, 75$).

(1SR,2SR,5RS,6SR)-1-Benzoyl-2,5,8-trimethyl-7,9-dioxo-8-azabicyclo[4.3.0]non-3-ene (24) (71%), m.p. 124–127 °C (from ether-light petroleum) (Found: C, 72.9; H, 6.5; N, 4.55. $\text{C}_{18}\text{H}_{19}\text{NO}_3$ requires C, 72.7; H, 6.45; N, 4.7%); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 1775 and 1705 (C=O), and 1600 cm^{-1} (aromatic ring); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.3 and 1.5 (each 3 H, d, J 7.3 Hz, 2 \times CHCH_3), 2.56 (1 H, m, 5-H), 3.02 (3 H, s, NMe), 3.22 (1 H, d, J 5 Hz, 6-H), 3.22 (1 H, m, 2-H), 5.68 and 5.74 (each 1 H, dt, J 9, 3 Hz, vinylic H), and 7.55 (5 H, m, aromatic H); m/z (C.I.) 298 ($M^+ + 1, 81\%$), 192 ($M^+ - 105, 100$), and 105 ($M^+ - 192, 47$).

(1SR,2SR,5RS,6SR)-1-(4-Methoxybenzoyl)-2,5,8-trimethyl-7,9-dioxo-8-azabicyclo[4.3.0]non-3-ene (25) (52%), m.p. 126–127 °C (from ether); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 1775 and 1705 (C=O), and 1605 cm^{-1} (aromatic ring); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.28 (3 H, d, J 7 Hz, CHCH_3), 1.48 (3 H, d, J 7.4 Hz, CHCH_3), 2.53 (1 H, m, 5-H), 3.02 (3 H, s, NMe), 3.20 (1 H, d, J 5.2 Hz, 6-H), 3.34 (1 H, m, 2-H), 3.85 (3 H, s, OMe), 5.67 and 5.72 (each 1 H, dt, J 9, 3 Hz, vinylic H), and 6.89 and 7.65 (each 2 H, m, aromatic H); m/z (E.I.) 327 (M^+ , 2%), 192 ($M^+ - 135, 100$), and 135 ($M^+ - 192, 98$).

(1SR,2SR,5RS,6SR)-1-(1-Oxopropyl)-2,5,8-trimethyl-7,9-dioxo-8-azabicyclo[4.3.0]non-3-ene (26) (12%), m.p. 59–60 °C (from ether-light petroleum) (Found: M^+ , 249.1366. $\text{C}_{14}\text{H}_{19}\text{NO}_3$ requires M , 249.1364); $\nu_{\max.}(\text{CH}_2\text{Cl}_2)$ 1770 and 1700 cm^{-1} (C=O); $\delta_{\text{H}}([\text{C}_6\text{H}_6]\text{benzene})$ 0.88 (3 H, t, J 7 Hz, CH_2CH_3), 1.30 and 1.37 (each 3 H, d, J 7.3 Hz, 2 \times CHCH_3), 1.80 (1 H, dq, J 19, 7 Hz, HCHCH_3), 2.13 (1 H, m, 5-H), 2.45 (1 H, dq, J 19, 7 Hz, HCHCH_3), 2.53 (1 H, d, J 5.7 Hz, 6-H), 2.63 (3 H, s, NMe), 2.92 (1 H, m, 2-H), and 5.38 and 5.44 (each 1 H, dt, J

9, 3 Hz, vinylic H); m/z (E.I.) 249 (M^+ , 2%) and 192 ($M^+ - 57$, 100).

(1SR,2SR,5RS,6SR)-1-(2-Methyl-1-oxopropyl)-2,5,8-trimethyl-7,9-dioxo-8-azabicyclo[4.3.0]non-3-ene (**27**) (29%), m.p. 73–76 °C (from ether–light petroleum) (Found: C, 68.1; H, 7.9; N, 5.4. $C_{15}H_{21}NO_3$ requires C, 68.4; H, 8.05; N, 5.25%); ν_{\max} (CH_2Cl_2) 3 050 (vinylic CH), and 1 770 and 1 700 cm^{-1} (C=O); δ_H ($[^2H_6]$ benzene) 0.76 (3 H, d, J 6.8 Hz, CHCH₃), 1.04 (3 H, d, J 6.6 Hz, CHCH₃), 1.31 (3 H, d, J 7.2 Hz, CHCH₃) 1.37 (3 H, d, J 7.4 Hz, CHCH₃), 2.16 (1 H, m, 5-H), 2.62 (3 H, s, NMe), 2.72 (1 H, h, J 6.7 Hz, CHMe₂), 2.75 (1 H, d, J 5.7 Hz, 6-H), 2.94 (1 H, m, 2-H), and 5.38 and 5.44 (each 1 H, dt, J 9, 3 Hz, vinylic H); m/z (E.I.) 264 ($M^+ + 1$, 1%), and 192 ($M^+ - 71$, 100).

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