(n = 0, R^1 = Me, R^2 = OH), 114908-71-3; (+)-**B** (n = 0, R^1 = Me, R^2 = OH), 114908-88-2; (±)-**B** (n = 1, R^1 = H, R^2 = Me), 114908-67-7; (±)-**B** (n = 2, R^1 = H, R^2 = Me), 114908-68-8; (±)-(R^*,R^*)-**B** (n = 0, R^1 = Me, R^2 = CH(Ph)$NHSO_2Ph$), 114908-69-9; (±)-(R^*,S^*)-**B** (n = 0, R^1 = Me, R^2 = CH(Ph)$NHSO_2Ph$), 114908-70-2; (±)-(R^*,R^*)-**B** (n = 1, R^1 = H, R^2 = CH(Ph)$NHSO_2Ph$), 114908-74-6; (±)-(R^*,S^*)-**B** (n = 1, R^1 = H, R^2 = CH(Ph)$NHSO_2Ph$), 114908-75-7; (±)-(R^*,R^*)-**B** (n = 2, R^1 = H, R^2 = CH(Ph)$NHSO_2Ph$), 114908-77-9; (±)-(R^*,S^*)-**B** (n = 2, R^1 = H, R^2 = CH(Ph)$NHSO_2Ph$), 114908-78-0; (±)-*cis*-**C** (n = 0, R^1 = R^2 = Me), 114908-63-3; (±)-*trans*-**C** (n = 0, R^1 = R^2 = Me), 114908-64-4; (±)-**C** (n = 0, R^1 = H, R^2 = Me), 114908-66-6; (±)-*cis*-**C** (n = 0, R^1 = Me, R^2 = OH), 114908-80-4; (±)-*trans*-**C** (n = 0, R^1 = Me, R^2 = OH), 114908-81-5; 2-(hydroxymethyl)-2-cyclopentenone, 68882-71-3; 2-(hydroxymethyl)-2-cyclohexenone, 105956-40-9; 2-(hydroxymethyl)-2-cycloheptenone, 114908-52-0; 2-(hydroxymethyl)-3-*n*-butyl-2-cyclopentenone, 114908-53-1; 2-(hydroxymethyl)-3-*n*-butyl-2-cyclohexenone, 114908-54-2; 2-(hydroxymethyl)-3-*n*-butyl-2-cycloheptenone, 114908-55-3; 2-(hydroxymethyl)-3-phenyl-2-cyclopentenone, 114908-56-4; 2-(hydroxymethyl)-3-phenyl-2-cyclohexenone, 114908-57-5; 2-(hydroxymethyl)-3-phenyl-2-cycloheptenone, 114908-58-6; 2-(hydroxymethyl)-3-vinyl-2-cyclopentenone, 114908-59-7; 2-(hydroxymethyl)-3-vinyl-2-cyclohexenone, 114908-60-0; 2-(hydroxymethyl)-3-vinyl-2-cycloheptenone, 114908-61-1; 2-lithio-2-ethyl-1,3-dithiane, 53178-38-4; 2-(hydroxymethyl)-3-(2-ethyl-1,3-dithian-2-yl)-2-cyclohexenone, 114929-05-4; 2-(hydroxymethyl)-3-(2-ethyl-1,3-dithian-2-yl)-2-cyclopentenone, 114929-06-5; 2-(hydroxymethyl)-3-(2-ethyl-1,3-dithian-2-yl)-2-cycloheptenone, 114908-62-2.

Diels–Alder Reactions of Cycloalkenones. 14. Endo Diastereoselectivity of 2-Cyclohexenones in Reactions with Cyclopentadiene[1]

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Aluminum chloride catalyzed Diels–Alder reactions of 2-cyclohexenones with cyclopentadiene are described. Structure analysis of the adducts by standard means and ^{13}C NMR spectroscopy is presented. The endo–exo diastereoselectivity of the above and earlier reactions is discussed.

A priori the two components of a Diels–Alder reaction may interact in two different orientations, affording endo and exo adducts. Often, however, only the endo adduct is formed. This fact was explained first by the Alder–Stein rule[3] of maximum accumulation of double bonds and later by stabilizing second-order orbital interactions,[4] inductive[5] or charge-transfer[6] interactions, and also geometrical overlap relationship of the π-orbitals at the primary centers.[7] Deviation from the endo rule was ascribed usually to steric factors.[8]

In a previous study[9] this aspect of the Diels–Alder reaction was investigated with catalyzed cycloadditions of 2-cyclohexenones with (*E*)-piperylene. The results showed that the presence of a methyl group at the olefinic α-carbon of the dienophile increases markedly the exo selectivity of the reaction. Whereas the reaction of 2-cyclohexenone is fully endo-selective, that of 2-methyl-2-cyclohexenone gives a 2.3:1 mixture of the endo and exo adducts. Similarly, the cycloadditions of 2-cyclohexenones substituted only at carbons 4 or 5 are fully endo-diastereoselective, but the reactions of the corresponding 2-methyl-2-cyclohexenones give mixtures of endo and exo adducts. A similar methyl effect was observed earlier in the thermal cycloadditions of dienophilic ethylenes with cyclopentadiene.[10–12]

In continuation of the above study, an investigation of aluminum chloride catalyzed reactions of cyclopentadiene

Table I. Aluminum Chloride Catalyzed Diels–Alder Reactions of Cyclohexenones 2–4 with Cyclopentadiene[a] and (*E*)-Piperylene[b]

	cyclopentadiene[d]			(*E*)-piperylene[d]	
dienophile	products	endo	exo	endo	exo
2a	**5a, 6a**	89	11	>97	
3a	**7a, 8a**	30	70	70[c]	30
2b	**5b, 6b**	95	5	>97	
3b	**7b, 8b**	60	40	>97	
2c	**5c, 6c**	79	21	>99	
3c	**7c, 8c**	29	71	>97	
4	**9, 10**	42	58	78	22

[a] Reaction conditions reported in Table III. [b] Reference 9. [c] Valenta and co-workers[13] reported a 78:22 mixture of endo and exo adducts for the reaction catalyzed by aluminum chloride. [d] Percent, GLC-based.

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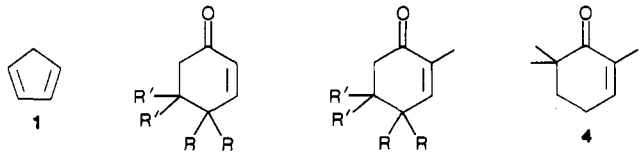
Table II. ^{13}C NMR Chemical Shifts of 5,8-Methanooctalones 5–10[a]

	5a	6a	5b	6b	5c	6c	7a	8a	7b	8b	7c	8c	9	10
C(1)	215.3	215.2	214.9	215.9	215.0	214.7	217.7	217.6	217.5	218.0	218.0	217.8	222.5	222.5
C(2)	39.2	39.1	35.6	35.5	53.7	53.7	37.8	37.5	35.3	34.8	52.3	51.5	42.4	43.4
C(3)	21.7	21.6	32.5	36.3	32.4	32.3	21.0	20.9	32.8	34.8	32.2	31.7	36.0	36.0
C(4)	27.9	29.6	31.2	32.5	41.4	43.3	28.7	30.2	31.8	32.7	42.5	44.4	24.8	26.8
C(4a)	41.3	41.3	50.2	48.9	37.8	37.2	49.5	48.6	58.6	58.4	46.0	44.4	49.7	49.0
C(5)	46.4	46.8	45.8	42.9	46.5[b]	47.1	46.9	48.1	46.7	44.4	47.5	49.4[b]	47.0	48.4
C(6)	134.7	137.3	134.9	140.0	136.4	137.1	134.1	138.4	134.9	139.8	136.2	137.3	134.4	138.3
C(7)	137.4	135.3	135.3	135.4	135.8	136.1	139.0	134.0	137.0	134.8	137.7	135.2	139.4	134.1
C(8)	45.0	44.0	47.0	42.0	46.2[b]	45.8	50.7	48.1	53.3	47.4	53.2	50.0[b]	51.1	48.4
C(8a)	51.5	50.1	51.0	51.6	49.8	49.0	55.3	53.8	54.2	52.4	52.9	52.3	55.5	54.3
CH_2	48.2	44.4	50.6	44.8	48.8	44.3	45.6	46.4	47.9	46.7	46.1	46.0	45.6	46.9
8a-Me							28.1	25.0	28.5	25.8	28.6	25.8	29.5	26.5
													25.0	26.1
2-Me														
													29.0	29.7
					31.4	31.6					33.0	33.3		
3-Me														
					27.6	27.0					27.6	27.9		
			30.7	21.9					30.6	22.2				
4-Me														
			27.8	31.7					28.7	32.2				

[a] The δ values are in parts per million downfield from Me_4Si: $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. [b] Signals in any vertical column may be interchanged.

(1) with 2-cyclohexenone (**2a**), 2-methyl-2-cyclohexenone (**3a**), 4,4-dimethyl-2-cyclohexenone (**2b**), 2,4,4-trimethyl-2-cyclohexenone (**3b**), 5,5-dimethyl-2-cyclohexenone (**2c**), 2,5,5-trimethyl-2-cyclohexenone (**3c**), and 2,6,6-trimethyl-2-cyclohexenone (**4**) was undertaken.



1 **2** **3** **4**

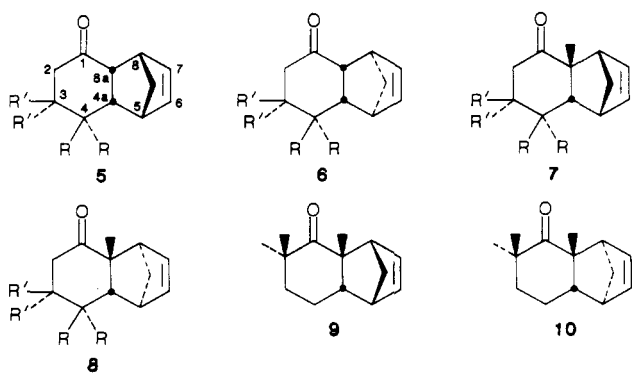
a, R = R′ = H; **b**, R = Me, R′ = H; **c**, R = H, R′ = Me

Diels–Alder Reactions and Products

The reactions of cyclopentadiene (1) with the seven dienophiles were performed under aluminum trichloride catalysis in dry toluene solution at 40 °C in various diene–dienophile combinations (Table III). The reaction products were mixtures of endo and exo adducts, as reported in Table I.

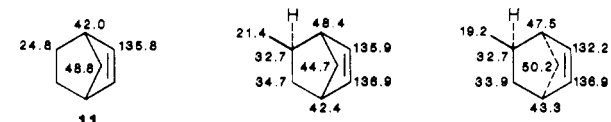
The reaction products were kinetically based Diels–Alder adducts, as shown by the constancy of the product ratios throughout the course of each reaction and the lack of endo–exo isomerization of the pure adducts on their exposure to the Diels–Alder reaction conditions.

The structures of the Diels–Alder adducts **5–10** were determined by ^{13}C NMR spectroscopy, the carbon shifts of these products being listed in Table II. The shift assignments followed routine ^{13}C NMR spectral analysis, shift comparison with the δ values recorded for the norbornenes **11–13** and their dihydro products,[14] and COSY and carbon–proton heteroatom correlation experiments.



5 **6** **7** **8** **9** **10**

a, R = R′ = H; **b**, R = Me, R′ = H; **c**, R = H, R′ = Me



11 **12** **13**

Several shifts and shift differences reveal the stereochemistry of the cycloaddition products. The 5,8-methano bridge is shielded (by ca. 4 ppm) more in the exo adducts (e.g., **6a** and **6c**) than in the endo compounds (e.g., **5a** and **5c**) as a consequence of a γ-effect exerted on the methylene group by either C(1) or C(4) in the exo adducts. Carbon-4 feels ca. 2 ppm more shielding in the endo compounds (**5a**, **5c**, **7a**, **7c**, and **9**) than in their exo counterparts (**6a**, **6c**, **8a**, **8c**, and **10**), presumably because of a stronger γ-effect from C(6) in the endo isomers than from the methano bridge in the exo isomers. As a shift comparison of endo adducts **5a–c** with their angularly methylated products **7a–c** indicates, the introduction of the 8a-methyl group leads to nearly 3 ppm shielding of the methano bridge, reflecting a γ-effect by the methyl group. The latter one-carbon unit is shielded by ca. 3 ppm in the exo adducts (**8a–c** and **10**) vs the endo equivalents (**7a–c** and **9**), presumably by a stronger γ-effect from C(7) in the exo isomers than from the methano bridge in the endo isomers. The introduction of a *gem*-dimethyl function into the endo or exo tricycles leads to shielding of the methylene or methine disposed 1,3 to the dimethylated carbon center within the ketone-bearing ring as a consequence of a γ-effect by the axial member of the pair of methyl groups (**5b–c** vs **5a**, **7b–c** and **9** vs **7a**, **6b–c** vs **6a**, **8b–c** and **10** vs **8a**).

Endo–Exo Diastereoselectivity

The product stereochemistry of the cycloadditions of cyclohexenones **2–4** with cyclopentadiene (1) and (*E*)-piperylene (i.e. earlier data[9]) are summarized in Table I.

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Inspection of the data shows the cycloadditions of cyclopentadiene (1) with the 2-cyclohexenones to be less endo-diastereoselective than those with (*E*)-piperylene. For example, the reaction of 2-cyclohexenone itself with (*E*)-piperylene is fully endo-diastereoselective, whereas the one with cyclopentadiene (1) affords an 8.1:1 mixture of endo and exo adducts.

The presence of a methyl group on the olefinic α-carbon of the α,β-unsaturated ketones increases the exo diastereoselectivity for the Diels–Alder reactions with cyclopentadiene (1). The reactions of the same ketones with (*E*)-piperylene show a different behavior.

Finally, comparison of the data for the trimethylated 2-cyclohexenones **3b**, **3c**, and **4** with those of 2-methyl-2-cyclohexenone (**3a**) reveals *gem*-dimethyl groups to increase the endo stereoselectivity in the reactions with (*E*)-piperylene. Contrastingly, in the cycloadditions with cyclopentadiene (1), the *gem*-dimethyl unit does not affect the endo stereoselectivity uniformly, the stereochemical outcome depending on the position of the methyl groups in the cyclohexenone ring.

These facts point out how complex the relationship is between dienophile structure and endo selectivity in the cycloadditions with cyclopentadiene and (*E*)-piperylene. The effect of the olefinic methyl group of 2-methyl-2-cyclohexenones upon the endo diastereoselectivity represents the most important aspect of the structure–selectivity relationship.

A marked "α-methyl effect" upon the endo diastereoselectivity has been observed already in the cycloadditions of cyclopentadiene with some ethylenic dienophiles, but the explanation of this effect has been fairly controversial.[10-12,15] A rationale for the endo–exo diastereoselectivity observed in the present, catalyzed reactions of 2-cyclohexenones with cyclopentadiene (1) had to be based on the following assumptions. The cycloadditions take place in a one-step reaction with an unsymmetrical, nonsynchronous transition state in which σ-bond formation with the β-carbon of the α,β-unsaturated ketone is in advance of that at the α-carbon site and the diene attack at the dienophile's β-carbon occurs (in the absence of strong steric interaction) along a direction antiparallel to the pseudoaxial bond at the cyclohexenone γ-carbon.[16] Under these circumstances the interplay between the repulsive destabilizing, steric interaction of the α-methyl group with the cyclopentadiene methylene hydrogens and the attractive secondary orbital interaction in the endo transition state controls the endo–exo diastereoselectivity. This explanation of the "α-methyl effect" seems to be of general validity for the reactions of cyclopentadiene (1) with acyclic and cyclic dienophiles.

It is noteworthy that the energy difference of endo and exo transition states in a highly endo-diastereoselective reaction (e.g., with a 99:1 endo–exo product ratio) is ca. 3 kcal/mol, causing even modest steric, nonbonded interactions to affect strongly the endo diastereoselectivity. The cycloadditions of 2-cyclohexenones with (*E*)-piperylene are more endo-diastereoselective than those with cyclopentadiene because of weaker steric, repulsive interaction of the enone α-methyl group with the (*E*)-piperylene methyl function in the endo transition state. Adoption of an unsymmetrical transition state, assumed heretofore for the Diels–Alder reactions of cycloalkenones, lends support to this rationalization in view of the steric interaction of the cyclopentadiene methylene group being influenced only weakly by the transition-state geometry and that of the (*E*)-piperylene methyl function being smaller in an unsymmetrical transition state than in a symmetrical one.

The presence of a *gem*-dimethyl group in the α-methylcyclohexenones affects the endo product formation in the reaction with cyclopentadiene (1) in a nonuniform manner, the extent of the effect depending on the position of the *gem*-dimethyl function. At carbons 4 and 6 the endo diastereoselectivity is increased, whereas at carbon 5 it is not affected. In the latter case the diene antiparallel attack is unfavorable because of the strong 1,3-diaxial interaction between the 5-axial methyl group and the developing bond at the β-carbon site and the nonbonded, steric interactions between the 5-axial methyl group and the cyclopentadiene in both endo and exo transition states. Hence, the cycloaddition occurs by a parallel diene approach at the β-carbon creating an incipient, fused cyclohexanone ring in half-boat conformation. In this event the C-5 methyl groups influence the stabilities of neither endo nor exo transition state.

Conclusions

The influence of an alkyl group at the olefinic α-carbon of the dienophile on the endo diastereoselectivity of the Diels–Alder reaction may be explained in terms of the interplay of stabilizing, secondary orbital interactions and substituent steric repulsive effects in the endo transition state. Although a quantitative assessment of these two opposing effects is not possible at this time, the present observations may be useful in predicting the stereochemical outcome of Diels–Alder reactions.

Experimental Section

Infrared spectra were measured in CCl_4 solution. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 300 and 75.5 MHz, respectively. Mass spectra were recorded at 70 eV and calibrated with perfluorotributylamine. Analytical GLC was carried out with a Carlo Erba HRGC-5160 (with an "on column" injection system on either an 0.32-mm × 30-m SP-2340 fused silica capillary column or a 0.25-mm × 30-m SPK-5 capillary column (internal standard: m-methoxyacetophenone). Absorption chromatography was carried out on Merk silica gel (0.040–0.063 mm, 230–400-mesh ASTM). Melting points are uncorrected. Cyclopentadiene was obtained by cracking dicyclopentadiene at 170 °C. The reactions were monitored by GLC.

General Procedure for the Diels–Alder Reactions. A solution of 2.4 g (25 mmol) of 2-cyclohexenone (**2a**) in 100 mL of dry toluene was added to a solution of 0.83 g (6.25 mmol) of aluminum chloride in 100 mL of dry toluene and the reaction mixture was stirred under nitrogen at room temperature for 40 min. Cyclopentadiene (9.9 g, 150 mmol) and enough solvent to produce a final solution of 250 mL were added (all operations being executed in a drybox), and the mixture was heated at 40 °C for 7 h. The cooled solution was poured into ice–water and extracted with ether. The extract was washed with 10% sodium bicarbonate solution and saturated brine, dried (Na_2SO_4), and evaporated under vacuum. Dissolution of the residual oil with pentane caused precipitation of a material of unknown constitution, which was filtered. Evaporation of the filtrate and two more pentane treatments led to 3.8 g of crude reaction product. Chromatography of the latter on 250 g of silica and elution with 9:1 pentane–ether gave octalones **5a** and **6a**.

The conditions for the reactions of all 2-cyclohexenones are detailed in Table III.

Octalone 5a: IR 3060 (w, olefinic CH), 1708 (s, C=O) cm^{-1}; ^1H NMR δ 0.7–0.9 (m, 1, H-4), 1.31 (br d, 1, J = 8 Hz, CH_2 bridge H), 1.45 (dt, 1, J = 8, 2 Hz, CH_2 bridge H), 1.6–1.8 (m, 2, C-3 Hs), 1.8–1.9 (m, 1, H-2), 1.9–2.0 (m, 1, H-4), 2.31 (ddt, 1, J = 18, 6,

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Table III. Reaction Conditions of the Diels–Alder Reactions of Cyclopentadiene (1) with Cyclohexenones 2–4 Catalyzed by Aluminum Chloride[a,b]

ketone	diene/ ketone[c]	$AlCl_3$/ ketone[c]	reactn time (h)	product yields (%, GLC-based)
2a	6	0.25	7	80
3a	15	0.25	20	70
2b	6	0.25	7	92
3b	27[d]	0.5	31	57
2c	6	0.25	7	99
3c	15	0.25	21	91
4	15	0.25	14	63

[a] Complexation time: 40 min, room temperature.[17,18] [b] Reaction temperature: 40 °C. [c] In equivalents. [d] In three additions of cyclopentadiene: 15 equiv initially, 6 equiv after 8 h and 6 equiv after 22 h.

2 Hz, eq H-2), 2.6–2.7 (m, 1, H-4a), 2.73 (dd, 1, J = 10, 4 Hz, H-8a), 2.88 (br s, 1, H-5), 3.26 (br s, 1, H-8), 6.01 (dd, 1, J = 6, 3 Hz, H-6), 6.17 (dd, 1, J = 6, 3 Hz, H-7); MS, m/e (relative intensity) 162 (M^+, 4), 97 (49), 91 (13), 79 (9), 78 (6), 77 (9), 68 (9), 67 (9), 66 (base), 65 (14), 51 (8). (2,4-Dinitrophenyl)hydrazone: mp 180–181 °C. Anal. Calcd for $C_{17}H_{18}N_4O_4$: C, 59.64; H, 5.30; N, 16.36. Found: C, 59.70; H, 5.34; N, 16.48.

Octalone 6a: IR 3060 (w, olefinic CH), 1705 (s, C=O) cm^{-1}; ^1H NMR δ 0.8–1.0 (m, 1, H-4), 1.17 (d, 1, J = 9 Hz, CH_2 bridge H), 1.29 (br d, 1, J = 9 Hz, CH_2 bridge H), 1.7–1.9 (m, 1, H-3), 1.9–2.0 (m, 1, H-3), 2.0–2.1 (m, 2, H-4, H-4a), 2.02 (s, 1, H-8a), 2.21 (ddd, 1, J = 18, 11, 8 Hz, H-2), 2.46 (dd, 1, J = 18, 8 Hz, H-2), 2.61 (br s, 1, H-5), 3.32 (br s, 1, H-8), 6.10 (dd, 1, J = 6, 3 Hz, H-7), 6.17 (dd, 1, J = 6, 3 Hz, H-6); MS, m/e (relative intensity) 162 (M^+, 2), 97 (52), 91 (15), 84 (8), 79 (11), 78 (7), 77 (10), 68 (7), 67 (9), 66 (base), 65 (13), 51 (7). (2,4-Dinitrophenyl)hydrazone: mp 190–191 °C. Anal. Calcd for $C_{17}H_{18}N_4O_4$: C, 59.64; H, 5.30; N, 16.36. Found: C, 59.80; H, 5.27; N, 16.40.

Octalone 7a: IR 3060 (w, olefinic CH), 1705 (s, C=O) cm^{-1}; ^1H NMR δ 1.30 (s, 3, C-8a Me), 2.85 (br s, 2, H-5, H-8), 5.98 (dd, 1, J = 6, 3 Hz, H-6), 6.17 (dd, 1, J = 6, 3 Hz, H-7); MS, m/e (relative intensity) 176 (M^+, 3), 111 (47), 93 (7), 91 (12), 82 (8), 79 (7), 77 (11), 67 (10), 66 (base), 65 (13), 55 (7), 54 (6), 53 (7), 51 (7). (2,4-Dinitrophenyl)hydrazone: mp 135–136 °C. Anal. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.65; N, 15.72. Found: C, 60.61; H, 5.81; N, 15.56.

Octalone 8a: IR 3060 (w, olefinic CH), 1705 (s, C=O) cm^{-1}; ^1H NMR δ 1.01 (s, 3, C-8a Me), 2.50 (br s, 1, H-5), 3.18 (br s, 1, H-8), 6.07 (m, 1, H-7), 6.27 (m, 1, H-6); MS, m/e (relative intensity) 176 (M^+, 0.4), 111 (58), 91 (10), 82 (7), 79 (6), 77 (10), 67 (10), 66 (base), 65 (11), 55 (6), 53 (6). (2,4-Dinitrophenyl)hydrazone: mp 144–145 °C. Anal. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.65; N, 15.72. Found: C, 60.80; H, 5.57; N, 15.80.

Octalone 5b: IR 3065 (w, olefinic CH), 1705 (s, C=O) cm^{-1}; ^1H NMR δ 0.94, 1.04 (s, 3 each, methyls), 1.30 (d, 1, J = 8 Hz, CH_2 bridge H), 1.42 (d, 1, J = 8 Hz, CH_2 bridge H), 1.5–1.7 (m, 2, H-2, H-3), 1.9–2.1 (m, 1, H-3), 2.30 (dd, 1, J = 10, 2 Hz, H-4a), 2.3–2.5 (m, 1, H-2), 2.83 (dd, 1, J = 10, 4 Hz, H-8a), 2.98 (br s, 1, H-5), 3.23 (br s, 1, H-8), 6.0–6.1 (m, 2, H-6, H-7); MS, m/e (relative intensity) 190 (M^+, 5), 126 (7), 125 (69), 97 (6), 91 (15), 81 (7), 79 (8), 77 (10), 69 (6), 67 (12), 66 (base), 65 (15), 55 (11), 53 (9), 51 (6). (2,4-Dinitrophenyl)hydrazone: mp 134–135 °C. Anal. Calcd for $C_{19}H_{22}N_4O_4$: C, 61.61; H, 5.98; N, 15.12. Found: C, 61.56; H, 5.80; N, 14.97.

Octalone 6b: IR 3060 (w, olefinic CH), 1712 (s, C=O) cm^{-1}; ^1H NMR δ 0.77, 1.09 (s, 3 each, methyls), 1.2–1.4 (m, 2, CH_2 bridge Hs), 1.6–1.7 (m, 1, H-3), 1.78 (d, 1, J = 11 Hz, H-4a), 1.8–1.9 (m, 1, H-2), 2.09 (d, 1, J = 11 Hz, H-8a), 2.3–2.4 (m, 2, H-2, H-3), 2.70 (br s, 1, H-5), 3.28 (br s, 1, H-8), 6.07 (dd, 1, J = 6, 3 Hz, H-7), 6.27 (dd, 1, J = 6, 3 Hz, H-6); MS, m/e (relative intensity) 190 (M^+, 3), 134 (16), 133 (11), 125 (67), 97 (32), 91 (20), 79 (13), 77 (10), 67 (12), 66 (base), 65 (14), 55 (12), 53 (8). (2,4-Dinitrophenyl)hydrazone: mp 133–134 °C. Anal. Calcd for $C_{19}H_{22}N_4O_4$: C, 61.61; H, 5.98; N, 15.12. Found: C, 61.70; H, 6.05; N, 15.20.

Octalone 7b: mp 104–105 °C; IR 3060 (w, olefinic CH), 1698 (s, C=O) cm^{-1}; ^1H NMR δ 0.97, 1.09 (s, 3 each, methyls), 1.37 (s, 3, C-8a Me), 1.4–1.5 (m, 2, CH_2 bridge Hs), 2.73 (br s, 1, H-5), 2.90 (br s, 1, H-8), 6.07 (br s, 2, H-6, H-7); MS, m/e 204 (relative intensity) (M^+, 2), 140 (6), 139 (64), 95 (11), 91 (10), 79 (7), 77 (9), 67 (15), 66 (base), 65 (11), 55 (9), 53 (6). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.86. Found: C, 82.26; H, 10.18.

Octalone 8b: mp 49–51 °C; IR 3060 (w, olefinic CH), 1708 (s, C=O) cm^{-1}; ^1H NMR δ 0.82, 1.08 (s, 3 each, methyls), 1.05 (s, 3, C-8a Me), 1.27 (br s, 1, H-4a), 1.31 (br s, 2, CH_2 bridge Hs), 2.63 (br s, 1, H-5), 3.10 (br s, 1, H-8), 6.07 (dd, 1, J = 5, 3 Hz, H-7), 6.28 (dd, 1, J = 5, 3 Hz, H-6); MS, m/e (relative intensity) 204 (M^+, 0.1), 140 (6), 139 (56), 105 (6), 95 (9), 91 (13), 79 (8), 77 (11), 67 (15), 66 (base), 65 (12), 55 (11), 53 (7). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.86. Found: C, 81.96; H, 9.95.

Octalone 5c: IR 3065 (w, olefinic CH), 1708 (s, C=O), 1655 (w, C=C) cm^{-1}; ^1H NMR δ 0.7–0.9 (m, 1, H-4), 0.93 (s, 3, eq Me), 1.01 (s, 3, ax Me), 1.36 (d, 1, J = 8 Hz, CH_2 bridge H), 1.48 (dt, 1, J = 8, 2 Hz, CH_2 bridge H), 1.68 (d, 1, J = 18 Hz, ax H-2), 1.7–1.8 (m, 1, H-4), 2.08 (dd, 1, J = 18, 3 Hz, eq H-2), 2.6–2.8 (m, 1, H-4a), 2.67 (d, 1, J = 3 Hz, H-8a), 2.90 (br s, 1, H-5), 3.28 (br s, 1, H-8), 6.11 (br s, 2, H-6, H-7); MS, m/e (relative intensity) 190 (M^+, 7), 125 (61), 91 (12), 79 (9), 77 (7), 69 (7), 68 (9), 67 (8), 66 (base), 65 (11), 55 (9). (2,4-Dinitrophenyl)hydrazone: mp 158–160 °C. Anal. Calcd for $C_{19}H_{22}N_4O_4$: C, 61.61; H, 5.98; N, 15.12. Found: C, 61.26; H, 5.91; N, 15.17.

Octalone 6c: IR 3055 (w, olefinic CH), 1702 (s, C=O) cm^{-1}; ^{1} H NMR δ 0.9–1.0 (m, 1, H-4), 1.03 (s, 6, methyls), 1.22 (d, 1, J = 9 Hz, CH_2 bridge H), 1.30 (br d, 1, J = 9 Hz, CH_2 bridge H), 1.86 (dd, 1, J = 13, 3 Hz, H-4), 2.0–2.1 (m, 2, H-4a, H-8a), 2.01 (d, 1, J = 18 Hz, ax H-2), 2.25 (dd, 1, J = 18, 3 Hz, eq H-2), 2.59 (br s, 1, H-5), 3.23 (br s, 1, H-8), 6.16 (m, 2, H-6, H-7); MS, m/e 190 (M^+, 1), 126 (6), 125 (64), 91 (14), 79 (9), 77 (8), 69 (6), 68 (9), 67 (8), 66 (base), 65 (12), 55 (10). (2,4-Dinitrophenyl)hydrazone: mp 148–149 °C. Anal. Calcd for $C_{19}H_{22}N_4O_4$: C, 61.61; H, 5.98; N, 15.12. Found: C, 61.47; H, 5.90; N, 15.01.

Octalone 7c: IR 3065 (w, olefinic CH), 1703 (s, C=O) cm^{-1}; ^1H NMR δ 0.82 (dd, 1, J = 13, 12 Hz, H-4), 0.93 (s, 3, eq Me), 1.10 (s, 3, ax Me), 1.42 (s, 3, C-8a Me), 1.43 (dt, 1, J = 9, 2 Hz, CH_2 bridge H), 1.63 (br d, 1, J = 9 Hz, CH_2 bridge H), 1.77 (ddd, 1, J = 13, 7, 3 Hz, H-4), 1.78 (d, 1, J = 18 Hz, ax H-2), 2.24 (dd, 1, J = 18, 3 Hz, eq H-2), 2.34 (ddd, 1, J = 12, 7, 4 Hz, H-4a), 2.82 (br s, 2, H-5, H-8), 6.11 (dd, 1, J = 5, 3 Hz, H-6), 6.16 (dd, 1, J = 5, 3 Hz, H-7); MS, m/e (relative intensity) 204 (M^+, 7), 139 (52), 93 (8), 91 (10), 82 (13), 79 (6), 77 (9), 69 (6), 67 (9), 66 (base), 65 (10), 55 (6), 54 (7), 53 (6). (2,4-Dinitrophenyl)hydrazone: mp 137–138 °C. Anal. Calcd for $C_{20}H_{24}N_4O_4$: C, 62.48; H, 6.23; N, 14.58. Found: C, 62.11; H, 6.19; N, 14.70.

Octalone 8c: IR 3060 (w, olefinic CH), 1700 (s, C=O) cm^{-1}; ^1H NMR δ 0.9–1.1 (m, 1, ax H-4), 1.03 (s, 3, eq Me), 1.08 (s, 3, C-8a Me), 1.14 (s, 3, ax Me), 1.29 (d, 1, J = 10 Hz, CH_2 bridge H), 1.33 (dd, 1, J = 10, 2 Hz, CH_2 bridge H), 1.66 (ddd, 1, J = 12, 7, 1 Hz, H-4a), 1.83 (ddd, 1, J = 14, 7, 3 Hz, eq H-4), 2.08 (d, 1, J = 18 Hz, ax H-2), 2.49 (dd, 1, J = 18, 3 Hz, eq H-2), 2.49 (br s, 1, H-5), 3.09 (br s, 1, H-8), 6.15 (dd, 1, J = 6, 3 Hz, H-7), 6.25 (dd, 1, J = 6, 3 Hz, H-6); MS, m/e (relative intensity) 204 (M^+, 1), 140 (7), 139 (68), 91 (10), 82 (12), 79 (6), 77 (9), 69 (7), 67 (9), 66 (base), 65 (9), 55 (6), 54 (7), 53 (6). (2,4-Dinitrophenyl)hydrazone: mp 185–186 °C. Anal. Calcd for $C_{20}H_{24}N_4O_4$: C, 62.48; H, 6.23; N, 14.58. Found: C, 62.40; H, 6.20; N, 14.50.

Octalone 9: IR 3060 (w, olefinic CH), 1700 (s, C=O) cm^{-1}; ^1H NMR δ 0.91, 1.11 (s, 3 each, methyls), 1.32 (s, 3, C-8a Me), 2.85 (br s, 2, H-5, H-8), 6.00 (m, 1, H-6), 6.12 (m, 1, H-7); MS, m/e (relative intensity) 204 (M^+, 2), 139 (50), 105 (8), 95 (22), 91 (14), 82 (49), 79 (9), 77 (12), 67 (11), 66 (base), 65 (12), 55 (9), 54 (13), 53 (9). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.86. Found: C, 82.28; H, 9.87.

Octalone 10: IR 3060 (w, olefinic CH), 1698 (s, C=O) cm^{-1}; ^1H NMR δ 1.01 (s, 3, C-8a Me), 1.11, 1.18 (s, 3 each, methyls), 2.45 (br s, 1, H-5), 3.22 (br s, 1, H-8), 6.03 (m, 1, H-7), 6.23 (m, 1, H-6); MS, m/e (relative intensity) 204 (M^+, 0.2), 139 (54), 105 (10), 95 (25), 91 (14), 82 (48), 79 (8), 77 (13), 67 (11), 66 (base), 65 (12), 55 (8), 54 (12), 53 (9). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.86. Found: C, 82.33; H, 9.88.

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