dinitrophenyl)hydrazone: mp 169-170 °C. Anal. Calcd for $C_{18}H_{22}O_4N_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.10; H, 6.15; N, 15.60.

Hydrogenation of the Octalones. A mixture of 200 mg of octalone and 20 mg of platinum oxide in 10 mL of dry ethanol was hydrogenated at room temperature and atmospheric pressure and the reaction terminated upon the consumption of an equimolar amount of hydrogen. The workup followed normal procedure.

Decalone 15: IR 1714 (s, C=O) cm^{-1}; ^1H NMR δ 0.88 (d, 3, J = 6 Hz, Me), 0.95 (d, 3, J = 6 Hz, Me). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.70; H, 11.15.

Decalone 16a: IR 1710 (s, C=O) cm^{-1}; ^1H NMR δ 0.97 (d, 3, J = 7 Hz, Me), 1.16 (s, 3, Me). The (2,4-dinitrophenyl)hydrazone: mp 147-148 °C. Anal. Calcd for $C_{18}H_{24}O_4N_4$: C, 59.98; H, 6.71; N, 15.54. Found: C, 60.04; H, 6.80; N, 15.46.

Decalone 16b: IR 1710 (s, C=O) cm^{-1}; ^1H NMR δ 1.05 (d, 3, J = 6 Hz, Me), 1.10 (d, 3, J = 7 Hz, Me), 1.25 (s, 3, Me). The (2,4-dinitrophenyl)hydrazone: mp 140-142 °C. Anal. Calcd for $C_{19}H_{26}O_4N_4$: C, 60.93; H, 7.01; N, 14.96. Found: C, 60.42; H, 6.99; N, 14.90.

Decalone 17a: IR 1710 (s, C=O) cm^{-1}; ^1H NMR δ 0.91 (d, 3, J = 7 Hz, Me), 1.15 (s, 3, Me). The (2,4-dinitrophenyl)hydrazone: mp 176-177 °C. Anal. Calcd for $C_{18}H_{24}O_4N_4$: C, 59.98; H, 6.71; N, 15.54. Found: C, 59.98; H, 6.70; N, 15.56.

Decalone 17b: IR 1710 (s, C=O) cm^{-1}; ^1H NMR δ 0.92 (d, 3, J = 7 Hz, Me), 1.10 (s, 3, Me), 1.33 (s, 3, Me). The (2,4-dinitrophenyl)hydrazone: mp 198-199 °C. Anal. Calcd for $C_{19}H_{26}O_4N_4$: C, 60.93; H, 7.01; N, 14.96. Found: C, 60.64; H, 6.95; N, 14.90.

Decalone 18: mp 28-29 °C; IR 1707 (s, C=O) cm^{-1}; ^1H NMR δ 1.10 (d, 3, J = 7 Hz, Me), 1.20 (d, 3, J = 7 Hz, Me). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.80; H, 11.12.

Decalone 19: mp 25-26 °C; IR 1715 (s, C=O) cm^{-1}; ^1H NMR δ 0.93 (d, 3, J = 7 Hz, Me), 1.10 (d, 3, J = 6 Hz, Me). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.75; H, 11.17.

Epimerization of Diels-Alder Adducts. A 0.1 M solution (6 mL) of sodium ethoxide in dry ethanol was added to a solution of 40 mg of cis bicyclic ketone in 8 mL of absolute ethanol under nitrogen and the mixture stirred at 22 °C for a length of time needed to establish equilibrium (as monitored by GC analysis).

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Diels-Alder Reactions of Cycloalkenones. 10. Endo-Exo Diastereoselectivity of 2-Cyclohexenones[1]

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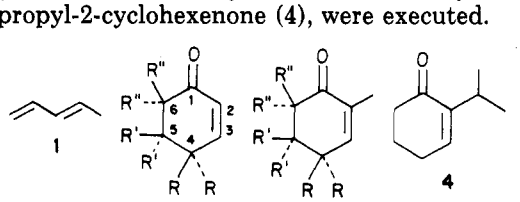
The Diels-Alder reactions of (*E*)-piperylene with 5,5-dimethyl-, 2,4,4-trimethyl-, 2,5,5-trimethyl-, 2,6,6-trimethyl-, and 2-isopropyl-2-cyclohexenone under aluminum chloride catalysis are described. Structure analysis of the adducts and some of their hydrogenation products by NMR spectroscopy is presented. The endo-exo diastereoselectivity of the above and earlier cycloadditions has been interpreted.

It has been known for some time that the Diels-Alder reactions of cyclopentadiene with acrolein, methyl vinyl ketone, and methyl acrylate lead preponderantly to endo products and that the endo-exo product ratio decreases seriously when the dienophiles are changed into methacrolein, methyl propenyl ketone, and methyl methacrylate, respectively.[3] A similar α-methyl effect was noticed during the broad study of the acid-catalyzed Diels-Alder reactions of cycloalkenones and (*E*)-piperylene (1), nearly exclusive endo addition being associated with C(2)-unsubstituted 2-cyclohexenones[1,4] but both endo and exo adducts resulting from reactions of 2-methyl-2-cyclohexenones.[1,4a,5] After a careful analysis of the diastereofacial selectivity of the cycloadditions of the cyclohexenones[1] it became of interest to examine their endo-exo diastereoselectivity, especially from the points of view of its dependence on conformational effects and the substitution pattern of the saturated ring carbons. Prior to consideration of the issue of diastereoisomerism the following additional Diels-Alder reactions of (*E*)-piperylene (1), i.e., cycloadditions with 5,5-dimethyl- (**2c**), 2,4,4-trimethyl- (**3b**), 2,5,5-trimethyl- (**3c**), 2,6,6-trimethyl- (**3d**) and 2-isopropyl-2-cyclohexenone (4), were executed.



Diels-Alder Reaction Products

The reactions of (*E*)-piperylene (1) with the five dienophiles were carried out under aluminum chloride catalysis in toluene solution at 40 °C for 8-90 h and led to 70-96% yields of octalones, as shown in Table III. 5,5-Dimethyl-2-cyclohexenone (**2c**) was converted into a 32:1 mixture of *trans*-octalone **5** and its 8a-epimer. The transformation

(1) For the previous paper, see: Angell E. C.; Fringuelli, F.; Pizzo, F.; Porter, B.; Taticchi, A.; Wenkert, E. *J. Org. Chem.*, preceding paper in this issue.

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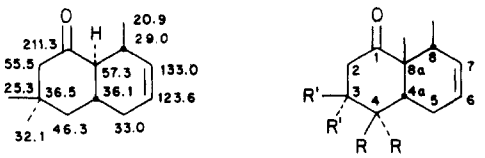
0022-3263/86/1951-2649$01.50/0

Table I. ^{13}C Chemical Shifts of *cis*-Octalones and *cis*-Decalones[a]

	cis-octalones						*cis*-decalones				
	6a	6b	7a	7b	8a	8b	10a[b]	10b	10c	10d	11
C(1)	217.2	215.7	221.4	217.2	215.9	213.8	215.0	216.7	216.7	220.4	215.8
C(2)	36.4	54.9	43.3	43.4	40.1	37.7	39.4	36.8[c]	53.8	44.8	40.3
C(3)	35.7	32.7	33.9	38.8	21.7	23.8	22.9	36.4[c]	30.4	35.5	22.6
C(4)	32.8	42.4	24.5	24.8	26.7	28.6	26.7[c]	33.9	41.6	23.9	26.6
C(4a)	50.0	35.1	36.1	41.5	36.1	34.3	47.5	55.8	42.3	45.6[c]	42.9
C(5)	23.3	28.1	28.3	29.0	28.6	29.7	29.0	25.6	29.6	29.8	29.6
C(6)	125.5	122.4	122.4	123.3	122.7	123.5	26.5[c]	27.0	21.5	26.3	26.4
C(7)	132.2	130.0	131.3	129.8	133.0	131.1	30.8	30.5	29.6	31.3	32.7
C(8)	37.5	36.7	38.8	30.3	33.4	31.2	42.9	42.0	39.5	45.3[c]	36.3
C(8a)	50.2	48.8	49.2	50.5	56.8	56.9	51.9	52.3	49.8	51.5	58.4
2-Me											
α			27.3[c]	28.2[c]						28.4[d]	
β			28.9[c]	29.0[c]						28.6[d]	
3-Me											
α		27.9							31.1[c]		
β		32.2							31.5[c]		
4-Me											
α	30.0[c]							30.5[d]			
β	31.0[c]							32.5[d]			
8-Me	16.9	21.3	18.8	14.6	19.1[c]	18.6[c]	16.7	18.0	18.3	17.8	20.2[c]
8a-Me	24.3	24.8	26.6[c]	15.9			23.9	26.7	25.2	24.9	
i-Pr Me					17.8	14.6					16.7
					19.4[c]	18.8[c]					19.4[c]
i-Pr CH					32.7	27.8					31.9

[a] The δ values are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. [b] From ref 4a and footnote 7 of ref 5. The shift assignment of carbons 3, 4, 5, and 7 required revision. [c,d] Signal in any vertical column may be reversed.

of 2,4,4-trimethyl- (**3b**) and 2,5,5-trimethyl-2-cyclohexenone (**3c**) led predominantly to *cis*-octalones **6a** and **6b**, respectively. Finally, the reaction of 2,6,6-trimethyl-2-cyclohexenone (**3d**) afforded a 3.5:1 mixture of *cis*-octalones **7a** and **7b** and that of 2-isopropyl-2-cyclohexenone (**4**) a 15.6:1 mixture of *cis*-octalones **8a** and **8b**. All octalones were kinetically based products, as indicated by the constancy of the product ratios of the first, fourth, and fifth reactions and the lack of endo–exo isomerization of ketones **6a** and **6b** during the course of their preparation.



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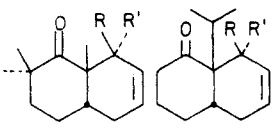
6a, R=Me, R'=H
b, R=H, R'=Me



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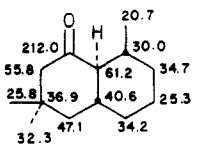
a, R=H, R'=Me
b, R=Me, R'=H



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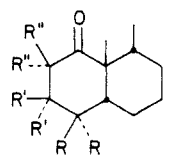
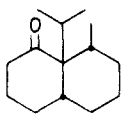


10a, R=R'=R"=H
b, R=Me, R'=R"=H
c, R=R"=H, R'=Me
d, R=R'=H, R"=Me



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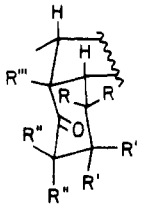
Base-induced isomerization of octalone **5** and decalone **9**, its product of hydrogenation, gave trans–cis mixtures of bicyclic ketones, the ratios being 49 and 19, respectively. The structures of the bicyclic ketones **5**–**8** and their dihydro derivatives were determined by ^{13}C NMR spectroscopy, the carbon shifts of the *cis*-octalones and -decalones being listed in Table I and those of the trans compounds appearing on their formulas.

The carbon shift assignment and structure analysis of the angular isopropyl compounds **8a**, **8b**, and **11** were based on the ^{13}C NMR data of their angularly methylated equivalents[1,4] and showed ketones **8a** and **11** to be in conformation **12** and bicycle **8b** in conformation **13**. The isopropyl group of ketones **8a** and **11** exhibits a rotamer preference as depicted in conformational structure **14** (for ketone **11**), as indicated by the strong shielding of carbons 4a and 8 (γ-effect), the deshielding of the 8-methyl group (δ-effect), and the shift dissimilarity of the isopropyl methyl shifts. The rotamer preference of the isopropyl group of ketone **8b**, indicated by the strong shielding of C(4a) (γ-effect), the deshielding of the 8-methyl group (δ-effect), and the sharp shift difference between the two isopropyl methyl functions, is shown in conformational formula **15**.



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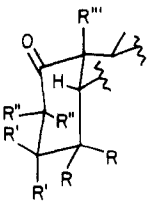

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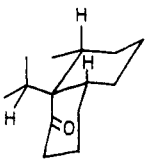

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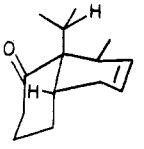


15

The shift data of ketones **6a** and **10b** favor them to exist preponderantly in conformation **12**, albeit not exclusively. Whereas this conformation is maintained to a large extent despite the unfavorable, 1,3-diaxial, nonbonded interaction between the 4β- and 8a-methyl groups, a similar nonbonded repulsion between the 2β- and 8a-methyl functions

Table II. Endo–Exo Diastereoselectivity of Reactions of 2-Cyclohexenones 2–4 with (*E*)-Piperylene (1)

dienophile	endo, %	exo, %	endo/exo
2a[a]	≥97		
4-alkyl-**2a**[b,c]	≥99		
5-alkyl-**2a**[b,d]	≥99		
6-methyl-**2a**[e]	≥99		
2b[a]	≥97		
2c	≥99		
3a[a]	70	30	2.3
4-methyl-**3a**[e]	79	21	3.8
5-isopropenyl-**3a**[f]	75	25	3
6-methyl-**3a**[e]	75	25	3
3b	≥97		>32
3c	≥97		>32
3d	78	22	3.5
4	94	6	15.6

[a] From ref 4a. [b] Alkyl = Me, *i*-Pr, or *t*-Bu. [c] From ref 4d. [d] From ref 4c. [e] From ref 1. [f] From ref 5.

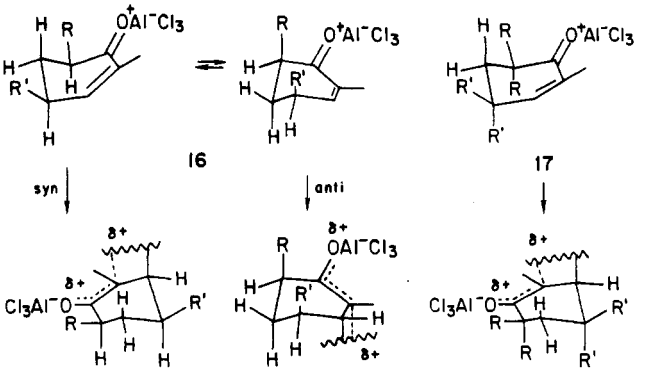
of ketones **7a** and **10d** may be responsible for the deformation of their ketonic rings (presumably by inversion into a twist-boat form) in conformation **12**. The δ values of ketones **6b** and **10c** are generally anomalous enough to suggest that these compounds may have both of their rings distorted (presumably the unfavorable, nonbonded interaction between the 3α-methyl group and C(5) being mainly responsible for this phenomenon) and that the ring deformations of the octalone may differ from those of the decalone. Finally, the ^{13}C NMR data of compound **7b** show this ketone to exist in solution in conformation **13** with ketonic ring distorted, presumably in twist-boat form (the 2α-methyl group repulsion of C(8) undoubtedly being the main cause for the deformation).

Endo–Exo Diastereoisomerism

Table II delineates the distribution of *endo* and/or *exo* products of cycloadditions encountered in the present and former studies. Four facts emerge from the data: (a) the uniformity and nearly exclusivity of endo addition of (*E*)-piperylene (1) and C(2)-unsubtituted 2-cyclohexenones,[6] (b) the production of 20–30% of exo adducts in Diels–Alder reactions of C(2)-methylated 2-cyclohexenone and its monoalkyl derivatives, (c) the suppression of the exo addition of the 4- and 5-methyl 2-methyl-2-cyclohexenones on introduction of a geminal methyl group in contrast to the lack of dissimilar behavior of 2,6-dimethyl- and 2,6,6-trimethyl-2-cyclohexenones, and (d) the appreciable reduction of exo addition on increase of the size of the 2-alkyl group.

As in the case of the interpretation of the diastereofacial selectivity of the acid-catalyzed Diels–Alder reactions of 2-cyclohexenones,[1] the following assumptions are a prerequisite for a rational analysis of the endo–exo diastereoselectivity of the reactions. The starting ketone–aluminum chloride complexes exist in a set of two envelope conformations, and the conformational equilibria are essentially the same as those of the ketones.[1] The Diels–Alder reactions take place in a one-step mechanism[7] with an unsymmetrical, nonsynchronous transition state[3a,7,8a] consisting of greater carbon–carbon σ-bond character at the β-carbon center of the α,β-unsaturated ketone than at the α-carbon site.[7e,f,8b] The diene–dienophile interaction at the β-carbon occurs with axial diene approach antiparallel to the pseudoaxial bond at the γ-carbon, forcing the incipient fused cyclohexanone into a half-chair conformation, in preference of a parallel approach, leading to an initial half-boat form for the same ring.[1]

Scheme I



Endo addition is considered generally the preferred stereochemical mode of the Diels–Alder reaction,[7f,9] frequently discussed as the favored reaction path on the basis of secondary orbital interactions stabilizing the endo transition state.[10] Thus the nearly exclusive endo addition of (*E*)-piperylene (1) to C(2)-unsubstituted 2-cyclohexenones represents an expected result. The low activation energy difference (up to 5 kcal/mol)[11a] between endo and exo cycloaddition leads to the expectation of slight variation of diene and/or dienophile structure causing significant changes in endo–exo diastereoselectivity. Hence the appearance of appreciable quantities of exo products in Diels–Alder reactions of 2-cyclohexenones modified structurally by the introduction of a 2-methyl group was not surprising, although the origin of this "2-methyl effect" has remained an unsolved issue. The observation of the same phenomenon in Diels–Alder reactions of cyclopentadiene with methyl isopropenyl ketone (in contrast to methyl vinyl ketone) and related dienophiles has led to the incompatible views of the 2-methyl effect being due to attractive nonbonded interaction between the 2-methyl substituent and the diene π-bonds in the exo transition state[3a] or to the nonbonded, diene–dienophile repulsion being greater in the endo than exo transition state.[3b,11] The present study sheds no new light on this subject.

In order to explain the dissimilarity of endo–exo diastereoselectivity of 2,4,4- (**3b**) and 2,6,6-trimethyl-2-cyclohexenone (**3d**), it is necessary to analyze conformationally each of their transition states in comparison with the transition states of 2,4-dimethyl- (4-methyl-**3a**) and 2,6-dimethyl-2-cyclohexenone (6-methyl-**3a**), respectively.

(6) For endo cycloadditions of 2-cyclohexenone with C(1)-substituted 1,3-butadienes other than (*E*)-piperylene, see: Overman, L. E.; Freerks, R. L.; Petty, C. B.; Clizbe, L. A.; Ono, R. K.; Tayler, G. F.; Hessup, P. J. *J. Am. Chem. Soc.* **1981**, 103, 2816. Kozikowsky, A. P.; Hurage, K.; Springer, J. P.; Wang, B. C.; Xu, Z. B. *Ibid.* **1984**, *106*, 1845.

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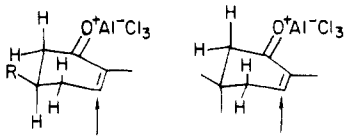
Table III. Reaction Conditions of the Diels–Alder Reactions of (*E*)-Piperylene (1) with 2-Cyclohexenones 2 and 3[a]

reactants	diene/ketone[b]	$AlCl_3$/ketone[b]	reaction time, h	products	product yield, %[c]	product ratio
1–2c	3	0.25	90	5,[c] 8a-*epi*-5[c]	95	32
1–3b	3	0.25	48	6a[d]	70	
1–3c	9	0.5	90	6b[d]	82	
1–3d	3	0.25	7.5	7a, 7b	96	3.5
1–4	15	0.9	50	8a, 8b	84	15.6

[a] Complexation time–40 min; complexation temperature–20 °C;[4a] ketone concentration–0.1 M; reaction temperature–40 °C. [b] Ratio of equivalents. [c] GC-based yields. [d] Plus up to 3% of unidentified material.

Scheme I protrays the reactions of the 2,6-dimethyl (**16a**) and 2,6,6-trimethyl (**17a**) compounds and indicates that the introduction of a geminal methyl group into the dimethylated nucleus does not influence the steric environment around the enone's β-carbon site. As a consequence the two substances exhibit similar cycloaddition reactivity (as shown qualitatively, by their Diels–Alder reaction rates[1]) and hence endo–exo diastereoselectivity (Table II).[7f,11c] Inspection of the conformational picture of the reactions of the 2,4-dimethyl (**16b**) and 2,4,4-trimethyl (**17b**) ketones (Scheme I) reveals that the introduction of the geminal methyl group removes the anti, low-energy pathway as an option for the cycloaddition thereby decreasing the reactivity of the trimethylated substance (once again, shown qualitatively by the Diels–Alder reaction rates[1]) and hence increasing its endo–exo diastereoselectivity (Table II).[7f,11c]

As the formulation **18** illustrates, the stereoelectronic anti addition of (*E*)-piperylene (1) to carvone (5-isopropenyl-**3a**; **18a**)[1,5] is precluded for the reaction of the diene with 2,5,5-trimethyl-2-cyclohexenone (**3c**; **18b**) in



18a 18b

view of the incipient creation of an axial carbon–carbon bond at the β-carbon center 1,3-diaxially to the 5-axial methyl group. Since, as a consequence, the latter ketone must undergo cycloaddition by way of a half-boat transition state, this ketone is less reactive than carvone (qualitative Diels–Alder reaction rates verifying this fact[1,5]) and thus much more endo diastereoselective (Table II).

Increasing the size of the 2-alkyl group of 2-alkyl-2-cyclohexenones would be expected for steric reasons to decrease the tendency toward exo product formation. This assumption is in agreement with the observation of much greater endo diastereoselectivity for 2-isopropyl-2-cyclohexenone (4) than 2-methyl-2-cyclohexenone (3) (Table II).

Experimental Section

The experimental details of the Diels–Alder reactions, of the hydrogenations, and of the base-induced product equilibrations as well as the specifics on the spectral analyses of all octalones and decalones and on the instruments used for the work are delineated in the Experimental Section of the preceding paper.[1] The carbon shifts on formulas **5** and **9** are in ppm downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. The 2,4-dinitrophenylhydrazones were recrystallized in 95% ethanol.

Diels–Alder Reactions. The reactions and their workup followed a previous prescription,[4a,12] and the conditions are detailed in Table III.

Octalone 5: IR 3020 (w, olefinic CH), 1710 (s, C=O), 1650 (w, C=C) cm^{-1}; ^1H NMR δ 0.88, 0.90 (s, 3 each, 2 Me), 1.02 (d, 3, *J* = 7 Hz, Me), 5.40 (m, 2, olefinic Hs). The (2,4-dinitrophenyl)hydrazone: mp 117–118 °C. Anal. Calcd for $C_{19}H_{24}O_4N_4$: C, 61.26; H, 6.51; N, 15.05. Found: C, 60.86; H, 6.59; N, 15.01.

Octalone 6a: IR 3020 (w, olefinic CH), 1705 (s, C=O), 1650 (w, C=C) cm^{-1}; ^1H NMR δ 0.95, 1.02, 1.22 (s, 3 each, 3 Me), 1.00 (d, 3, *J* = 7 Hz, Me), 5.82 (m, 2, olefinic Hs). The (2,4-dinitrophenyl)hydrazone: mp 147–148 °C. Anal. Calcd for $C_{20}H_{26}O_4N_4$: C, 62.15; H, 6.79; N, 14.50. Found: C, 61.91; H, 6.89; N, 14.33.

Octalone 6b: IR 3020 (w, olefinic CH), 1700 (s, C=O), 1655 (w, C=C) cm^{-1}; ^1H NMR δ 1.00 (d, 3, *J* = 6 Hz, Me), 1.02, 1.13, 1.15 (s, 3 each, 3 Me), 5.55 (br, s, olefinic Hs). The (2,4-dinitrophenyl)hydrazone: mp 152 °C. Anal. Calcd for $C_{20}H_{26}O_4N_4$: C, 62.15; H, 6.79; N, 14.50. Found: C, 62.22; H, 6.76; N, 14.37.

Octalone 7a:[13] IR 3020 (w, olefinic CH), 1702 (s, C=O), 1660 (w, C=C) cm^{-1}; ^1H NMR δ 0.98 (d, 3, *J* = 7 Hz, Me), 1.03, 1.17, 1.20 (s, 3 each, 3 Me), 5.53 (br, s, 2, olefinic Hs). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.70; H, 10.65.

Octalone 7b: IR 3020 (w, olefinic, CH), 1698 (s, C=O), 1658 (w, C=C) cm^{-1}; ^1H NMR δ 0.80 (d, 3, *J* = 7 Hz, Me), 0.95, 1.02, 1.16 (s, 3 each, 3 Me), 5.33 (m, 2, olefinic Hs). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.35; H, 10.80.

Octalone 8a: IR 3020 (w, olefinic CH), 1708 (s, C=O), 1390, 1370 (m, CMe_2) cm^{-1}; ^1H NMR δ 0.93 (d, 3, *J* = 7 Hz, Me), 0.97 (d, 3, *J* = 7 Hz, Me), 1.09 (d, 3, *J* = 7 Hz, Me), 5.47 (m, 2, olefinic Hs). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.74. Found: C, 81.58; H, 10.64.

Octalone 8b: IR 3020 (w, olefinic CH), 1705 (s, C=O), 1385, 1370 (m, CMe_2) cm^{-1}; ^1H NMR δ 0.85 (d, 3, *J* = 7 Hz, Me), 0.93 (d, 3, *J* = 7 Hz, Me), 0.98 (d, 3, *J* = 7 Hz, Me), 5.48 (m, 2, olefinic Hs). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.74. Found: C, 81.77; H, 10.78.

Decalone 9: IR 1710 (s, C=O) cm^{-1}; ^1H NMR δ 0.90, 0.90, 1.05 (s, 3 each, 3 Me). The (2,4-dinitrophenyl)hydrazone: mp 167 °C. Anal. Calcd for $C_{19}H_{26}O_4N_4$: C, 60.93; H, 7.01; N, 14.96. Found: C, 61.07; H, 7.10; N, 15.04.

Decalone 10a: IR 1700 (s, C=O) cm^{-1}; ^1H NMR δ 0.63 (d, 3, *J* = 7 Hz, Me), 1.00 (s, 3, Me). The (2,4-dinitrophenyl)hydrazone: mp 139–140 °C. Anal. Calcd for $C_{18}H_{24}O_4N_4$: C, 59.98; H, 6.71; N, 15.54. Found: C, 59.58; H, 6.74; N, 15.46.

Decalone 10b: IR 1710 (s, C=O) cm^{-1}; ^1H NMR δ 0.98, 1.35, 1.42 (s, 3 each, 3 Me), 1.14 (br s, 3, Me). The (2,4-dinitrophenyl)hydrazone: mp 157–158 °C. Anal. Calcd for $C_{20}H_{28}O_4N_4$: C, 61.68; H, 7.26; N, 14.42. Found: C, 61.74; H, 7.28; N, 14.53.

Decalone 10c: IR 1700 (s, C=O) cm^{-1}; ^1H NMR δ 1.02, 1.07, 1.30 (s, 3 each, 3 Me), 1.05 (d, 3, *J* = 6 Hz, Me). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.60; H, 11.65.

Decalone 10d: mp 56 °C; IR 1700 (s, C=O) cm^{-1}; ^1H NMR δ 1.00, 1.15, 1.20 (s, 3 each, 3 Me), 1.30 (d, 3, *J* = 7 Hz, Me). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.10; H, 11.60.

Decalone 11: IR 1705 (s, C=O), 1395, 1380 (m, CMe_2) cm^{-1}; ^1H NMR δ 0.97 (d, 3, *J* = 7 Hz, Me), 1.02 (d, 3, *J* = 7 Hz, Me), 1.13 (d, 3, *J* = 7 Hz, Me). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.78; H, 11.66.

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(12) For the preparation of starting 2-cyclohexenones **2c**, **3b**, **3c**, **3d**, and **4**, see (in sequential order): (a) Hiegel, A.; Burk, P. *J. Org. Chem.* **1973**, *38*, 3637. (b) Smith, H. A.; Huff, B. J. L.; Powers, W. J.; Caine, D. *J. Org. Chem.* **1967**, *32*, 2851. (c) Clark, R. D.; Ellis, J. E.; Hearthcock, C. H. *Synth. Commun.* **1973**, *3*, 347. Ellis, J. E.; Dutcher, J. S.; Heathcock, C. H. *J. Org. Chem.* **1976**, *41*, 2670. (d) Rubottom, G. M.; Juve, H. D., Jr. *Ibid.* **1983**, *48*, 422. (e) Larcheveque, M.; Valette, G.; Cuvigny, T. *Tetrahedron* **1979**, *35*, 1745.

(13) The 1–**3d** reaction has been reported earlier: Yoshida, T. U.S. Patent 4 339 467, 1982; *Chem. Abstr.* **1982**, *97*, 182019.