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Addition Reactions of Cyclic *s-trans*-Enaminones with Grignard Reagents.

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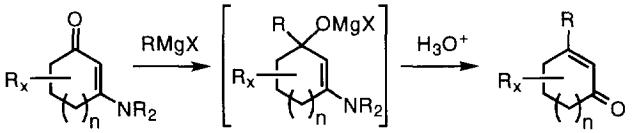
Abstract: Addition of Grignard reagents to *s-trans*-enaminones derived from 1,3-cycloalkanediones are described. In dichloromethane, addition of phenylmagnesium bromide gave 3-phenyl substituted cycloalkenones. Alkylmagnesium halides underwent multiple addition reactions, giving mixtures of the 3-alkylcycloalkenones and 1,3-dialkyl-3-(dialkylamino)cyclohexenes. In tetrahydrofuran, only the 3-alkylcycloalkenone was obtained.

Introduction

As part of a strategy for the synthesis of substituted cycloalkenones, the addition of organometallic compounds such as Grignard reagents to enaminones derived from cycloalkane-1,3-diones was envisioned. Hydrolysis of an initial 1,2 adduct was expected to give the desired cycloalkenone according to the reaction sequence shown in Scheme 1, previously established for alkoxy anologues of these substrates.[1]

Scheme 1



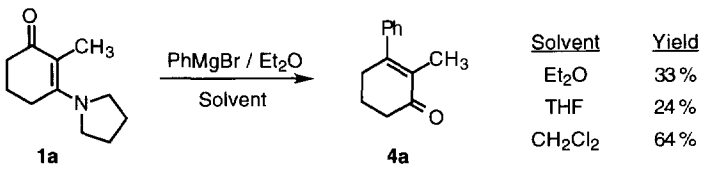
Despite the apparent simplicity of this reaction sequence and the significant body of research described of enaminones,[2] only a single report of an addition reaction of an organometallic nucleophile to a cyclic *s-trans*-enaminone has been found.[2c] In this case, alkyllithium reagents were described as reacting with cyclopentenaminones in hydrocarbon solvent by a 1,4 addition-elimination pathway, giving the 3-alkylcyclopentenone. The only other report[2a] specifically mentioning additions to *s-trans*-enaminones cited the *failure* of organometallic nucleophiles to add to enaminones derived from 1,3-cyclohexanedione. Meanwhile, addition reactions of cyclic *s-cis*-enaminones are well-documented.[3]

Results and Discussion

We have found that synthetically useful yields of cycloalkenones are obtained from the corresponding *s-trans*-enaminone by the addition of a Grignard reagent followed by hydrolysis according to Scheme 1.[4] A competitive process has also been identified in which two equivalents of the Grignard reagent react with the substrate enaminone, giving disubstituted aminocycloalkenes as *bis*-adducts (see below). The course of this reaction varies with solvent and Grignard reagent.

In the original test of the proposed reaction, enaminone **1a**[5a] was treated with an excess (3 equiv.) of an ethereal solution of phenylmagnesium bromide in either tetrahydrofuran, diethyl ether, or dichloromethane (Scheme 2). Although some addition did occur in ether and in THF, yields were low (33 and 24 %, respectively); in these cases the reaction mixture was heterogeneous and mixing of the reagents was impossible with magnetic stirring. However, use of dichloromethane as the solvent resulted in a clear homogeneous solution and aqueous workup gave 3-phenyl-2-methylcyclohexen-2-one[6] **4a** in 64 % isolated yield. We later found that reactions of *alkyl*magnesium halides in THF proceeded without incident.

Scheme 2



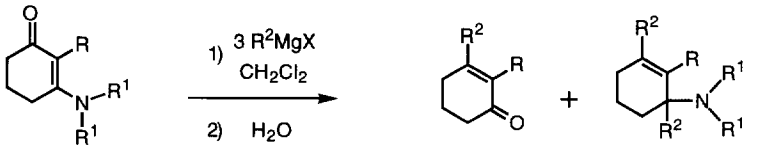
1a **4a**

Solvent	Yield
Et_2O	33 %
THF	24 %
CH_2Cl_2	64 %

These results prompted further exploration of this reaction as a function of the substrate, Grignard reagent, and solvent. Addition reactions of a variety of Grignard reagents were studied using various enaminones derived from cyclohexane-1,3-diones (Table 1, next page). Except as noted in Table 3, the Grignard reagent as a solution in diethyl ether was added to a solution of the substrate in a fourfold volume (relative to the volume of Grignard solution) of the indicated solvent.

Three equivalents of the Grignard reagent were used in order to permit the fullest possible extent of multiple addition. Nevertheless, the 3-alkylcyclohexenones[7] **4** were obtained in isolated yields as high as 90 %. Formation of aminocyclohexenes **5** was always seen with alkylmagnesium halides in methylene chloride, while phenylmagnesium bromide gave only the enone without regard to solvent. Formation of the aminocycloalkene is not seen in tetrahydrofuran, indicating a solvent selectivity for addition of alkylmagnesium halides.

Table 1



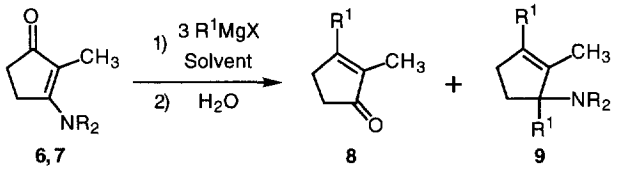
1-3 **4** **5**

Entry	Substrate	R	R^1	R^2MgX	Solvent	Yield (4 : 5)
1	**1a**	Me	$-CH_2CH_2CH_2CH_2-$	PhMgBr	CH_2Cl_2	**4a:5a** = 64:0[b]
2	**1a**	Me	$-CH_2CH_2CH_2CH_2-$	BuMgCl	CH_2Cl_2	**4b:5b** = 47:46
3	**1a**	Me	$-CH_2CH_2CH_2CH_2-$	BuMgCl	Et_2O	**4b:5b** = 75:4
4	**1a**	Me	$-CH_2CH_2CH_2CH_2-$	BuMgCl	THF	**4b:5b** = 65:0[b]
5	**1a**	Me	$-CH_2CH_2CH_2CH_2-$	EtMgCl	CH_2Cl_2	**4c:5c** = 33:65
6	**1a**	Me	$-CH_2CH_2CH_2CH_2-$	EtMgCl	THF	**4c:5c** = 55:0[b]
7	**1a**	Me	$-CH_2CH_2CH_2CH_2-$	EtMgBr	CH_2Cl_2	**4c:5c** = 62:15
8	**1b**	H	$-CH_2CH_2CH_2CH_2-$	BuMgCl	CH_2Cl_2	**4d:5d** = 47:36
9	**1b**	H	$-CH_2CH_2CH_2CH_2-$	PhMgBr	CH_2Cl_2	**4e:5e** = 81:0[b]
10	**2a**	Me	Et_2	BuMgCl	CH_2Cl_2	**4a:5f** = 36:47
11	**2a**	Me	Et_2	PhMgBr	CH_2Cl_2	**4b:5g** = 64:0[b]
12	**3a**	Me	$-CH_2CH_2OCH_2CH_2-$	BuMgCl	CH_2Cl_2	**4a:5h** = 80:15
13	**3a**	Me	$-CH_2CH_2OCH_2CH_2-$	BuMgCl	THF	**4a:5h** = 84:0[b]
14	**3a**	Me	$-CH_2CH_2OCH_2CH_2-$	PhMgBr	CH_2Cl_2	**4b:5i** = 90:0[b]
15	**3b**	H	$-CH_2CH_2OCH_2CH_2-$	BuMgCl	CH_2Cl_2	**4d:5j** = 34:42
16	**3b**	H	$-CH_2CH_2OCH_2CH_2-$	BuMgCl	THF	**4d:5j** = 51:0[b]
17	**3b**	H	$-CH_2CH_2OCH_2CH_2-$	PhMgBr	CH_2Cl_2	**4e:5k** = 72:0[b]

Note: (a) Yields are of products isolated by chromatography on silica gel and are unoptimized.
(b) None of the *bis*-adduct **5** was detected.

These trends in reactivity have also been found to apply to the five-membered analogues **6** and **7**. In these reactions, the major products were 3-alkylcyclopentenones[8] **8** (Table 2). Again, use of dichloromethane as solvent resulted in the formation of a significant amount of the aminocyclopentene **9**, while use of THF as solvent resulted in exclusive formation of the 3-alkylcyclopentenone. Although aminocycloalkenes **5** and **9** exhibited sensitivity to acid (silica gel) and heat (gas chromatography), analytically pure samples were obtained chromatographically using triethylamine-deactivated silica gel.

Table 2



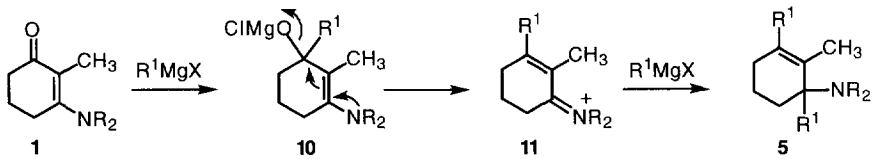
6,7 8 9

Entry	Substrate	R	R¹MgX	Solvent	Yield (**8** : **9**)
1	**6**	-$CH_2CH_2CH_2CH_2$-	BuMgCl	CH_2Cl_2	**8a:9a** = 41:30
2	**6**	-$CH_2CH_2CH_2CH_2$-	BuMgCl	THF	**8a:9a** = 85:0[b]
3	**6**	-$CH_2CH_2CH_2CH_2$-	PhMgBr	CH_2Cl_2	**8b:9b** = 38:0[b]
4	**6**	-$CH_2CH_2CH_2CH_2$-	PhMgBr	THF	**8b:9b** = 79:0[b]
5	**7**	-$CH_2CH_2OCH_2CH_2$-	BuMgCl	CH_2Cl_2	**8a:9c** = 50:30
6	**7**	-$CH_2CH_2OCH_2CH_2$-	BuMgCl	THF	**8a:9c** = 75:0[b]
7	**7**	-$CH_2CH_2OCH_2CH_2$-	PhMgBr	CH_2Cl_2	**8b:9d** = 80:0[b]

Note: (a) Yields are of products isolated by chromatography on silica gel and are unoptimized.
(b) None of the *bis*-adduct **9** was detected.

We propose the mechanism shown in Scheme 3 to account for the formation of these products. Loss of oxymagnesium halide from an initial 1,2-adduct gives an intermediate iminium ion **10**. Although loss of $XMgO^-$ is unusual, dissociation of halide from $XMgO^-$ would give neutral magnesium oxide. Similar multiple addition reactions are observed in hydride reductions and reactions of Grignard reagents with tertiary amides[9a] and lactams,[9b] of which **1-3**, **6** and **7** are vinylogous analogues. In addition, formation of the aminocyclohexenes in yields as high as 65 % suggests that addition occurs initially at the carbonyl group, rather than the 1,4-addition described of alkyllithiums. Reaction of either **10** or **11** with water upon workup would give the corresponding cycloalkenone.

Scheme 3



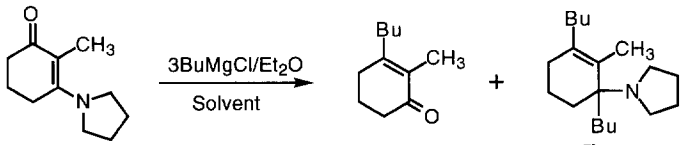
1 10 11 5

In only one case was the aminocycloalkene **5** formed in significant excess (Table 1, Entry 5), and no distinct trends appear to result from variation of the amino group. Only where R = methyl (**3a**; Table 1, Entry 12) does the morpholinyl group appear to influence the course of the reaction, compared to the corresponding diethylamino and pyrrolidinyl substrates (Entries 2 and 10). In the reaction of **3a**, steric hindrance by the allylic methyl group combined with the less electron-donating nature of the morpholinyl group would retard the formation of **11**, giving less of the *bis*-adduct **5** (15 %, compared to 46 and 47 %).

The possibility exists that aminocycloalkenes arise by conversion of **10** to iminium ion **11** during workup, followed by reaction with unhydrolyzed Grignard reagent.[10] This was addressed in the reaction of **1a** with butylmagnesium chloride in dichloromethane followed by slow addition of the reaction mixture to excess aqueous HCl, basification and extraction into ether. This procedure did not alter the product ratio. Further, attempts to limit the amount of multiple addition by varying the stoichiometry of the reaction failed: when 1.2 equivalents of butylmagnesium chloride was reacted with **1a**, enone **4b** was obtained (40 %) along with a significant amount of aminocyclohexene **5b** (26 %).

It is proposed that the observed solvent selectivity is due to an interplay between the polarity and coordinating ability of the solvent. Polarity is not the sole criterion in determining whether or not the *bis*-adduct forms. Dichloromethane is the most polar of the three solvents studied, and supports formation of the intermediate iminium ion **11** and the *bis*-adduct derived therefrom. Even though it is of intermediate polarity, tetrahydrofuran gave no *bis*-adduct except under forcing conditions. Diethyl ether allowed for the formation of a small amount of the *bis*-adduct despite the fact that it is the least polar of the three solvents. These trends are seen among Entries 2-4 of Table 1. We hypothesize that the coordination of THF to the Mg atom stabilizes the 1,2-adduct **10**, impeding its decomposition to **11** and resulting in a diminution of the *bis*-adduct. To test this hypothesis, substances with recognized metal-coordinating abilities were added to the reaction under the surmise that they would reduce the amount of *bis*-adduct being formed. Table 3 shows the results of these and other variations in reaction conditions.

Table 3



1a **4b** **5b**

Entry	Additive	Solvent	Conditions	Yield (**4b** : **5b**)
1	None	CH_2Cl_2	r.t., 18h	47 : 46
2	$3Et_3N$	CH_2Cl_2	r.t., 18h	68 : 19
3	3HMPA	CH_2Cl_2	r.t., 18h	54 : 22
4	None	CH_2Cl_2	reflux, 18h	26 : 57
5	None	THF	reflux, 18h	57 : 14
6*	None	CH_2Cl_2*	r.t., 18h	34 : 43
7*	$MgCl_2$	CH_2Cl_2*	r.t., 18h	21 : 53

* Ether evaporated *in vacuo* prior to addition of CH_2Cl_2 and substrate.

Entries 1-3 of Table 3 show the effects of an equimolar amount (with respect to BuMgCl) of triethylamine and hexamethylphosphoramide on the product ratio. These were added to the reaction prior to

the Grignard reagent. In each case a decrease in the amount of *bis*-adduct was observed, supporting the hypothesis that coordinative saturation of the Mg atom retards formation of the *bis*-adduct.

Some other variations in reaction conditions are also illustrated in Scheme 3. For instance, carrying out the reaction in refluxing dichloromethane (Entry 4) results in an increase in the amount of *bis*-adduct, although the enone persists. As mentioned earlier, tetrahydrofuran does permit the formation of a small amount of *bis*-adduct under forcing conditions (Entry 5). An attempt to increase the amount of *bis*-adduct was also made by adding anhydrous $MgCl_2$ to the reaction mixture after evaporation of ether from the Grignard reagent *in vacuo*. It was thought that the added Lewis acid would sequester ether molecules from the coordination sphere of the magnesium atom of **10**, thereby promoting its decomposition to imminium ion **11** and formation of the *bis*-adduct. Although this modification gives a slight increase in the amount of *bis*-adduct, a comparison of Entries 6 and 7 shows that the effect is limited.

An alternative explanation for these observations centers on the state of aggregation of the magnesium atom of **10**. Although there is some debate as to the nature of Grignard reagents in solution, they are thought to exist as dimers and in equilibrium with diorganomagnesium species via the Schlenk equilibrium.[11] Highly coordinating solvents such as tetrahydrofuran or Lewis basic additives promote a monomeric organomagnesium species.[11b] Thus, the increase in production of the *bis*-adduct in dichloromethane and diethyl ether appears to correlate with the higher degree of aggregation found in these solvents. This trend is not followed in reactions of phenylmagnesium bromide, which has also been found to exist as an aggregate in solution.[11c] At present, it is not known why the *bis*-adduct does not form on addition of phenylmagnesium bromide, although benzylic stablilization of the intermediate iminium ion **11** could result in a marked decrease in its reactivity. Hydrolysis of **11** on workup would provide phenyl-subsituted cyclohexenone **4a**.

To summarize, it has been found that Grignard reagents readily add to cyclic *s-trans*-enaminones and that 3-alkylcycloalkenones **4** and **8** can be isolated in good to excellent yields.[1] These cycloalkenones correspond to those that would be obtained via the Stork-Danheiser procedure. A second addition takes place in some instances to give *bis*-adducts **5** and **9**. Factors that have been identified as influencing this process include solvent polarity and coordinating ability. While cycloalkenones can be obtained selectively and in moderate to high yields using this method, it would be desirable to optimize formation of the *bis*-adduct. More highly functionalized examples of these are seen as precursors to alkaloid natural products. Results of these efforts will be described in due course.

Experimental Section

General.

Pyrrolidinyl and morpholinyl derivatives of the 1,3-cycloalkanediones were prepared as described by Iida *et al.*[5a] The diethylamino derivative of 2-methyl-1,3-cyclohexanedione was prepared by the modification described by Baraldi *et al.*[5b] Grignard reagents were purchased from Aldrich Chemical Co. and titrated with 2,5-dimethoxybenzyl alcohol using 1,10-phenanthroline as an indicator. TLC analysis was performed on silica gel plates (Whatman 4420-220) and visualized by charring with 5 % vanillin in 5 % H_2SO_4 - ethanol. Proton NMR spectra were recorded at 300 MHz using residual $CHCl_3$ (7.26 ppm) as an internal standard. Combustion analyses were performed by M-H-W Laboratories, Phoenix, AZ.

2-Methyl-3-diethylamino-2-cyclohexen-1-one (2a). Prepared by the method of Baraldi *et al.*[5b] from 4.492 g (35.61 mmol, 1.0 equiv.) 2-methyl-1,3-cyclohexanedione, 7.7 mL (74 mmol, 2.1 equiv.) diethylamine, and 5.1 mL (89 mmol, 2.5 equiv.) glacial acetic acid in 110 mL toluene. The product was isolated by Kugelrohr distillation (62-67 °C, 0.03 mm Hg) as a clear yellow oil (3.87 g, 59.9 %). ^{1}H NMR ($CDCl_3$) δ: 1.12 (t, 6H, J = 7.2 Hz); 1.78 (m, 3H); 1.81 (pentet, 2H, J = 6.6 Hz); 2.27 (apparent triplet, 2H, J = 6.1 Hz); 2.46 (broad triplet, 2H, J = 6.4 Hz); 3.25 (q, 4H, J = 7.1 Hz). IR (CH_2Cl_2): 1625 cm^{-1}. Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56. Found: C, 72.67; H, 10.42.

2-Methyl-3-(4-morpholinyl)-2-cyclohexen-1-one (3a). Prepared by the method of Iida *et al.*[5a] from 2.504 g (19.85 mmol, 1.0 equiv.) of 2-methyl-1,3-cyclohexanedione and 1.9 mL (22 mmol, 1.1 equiv.) of morpholine in 50 mL of toluene. The title compound was isolated by Kugelrohr distillation (90-100 °C, 0.05 mm Hg) giving 3.24 g (83.6 %) of a clear, pale yellow oil which crystallized on standing, m.p. 66 - 68 °C. ^{1}H NMR ($CDCl_3$) δ: 1.77 (t, 3H, J = 1.4 Hz); 1.83 - 1.91 (m, 2H); 2.30 (apparent triplet, 2H, J = 7.2 Hz); 2.42 - 2.47 (m, 2H); 3.19 (apparent triplet, 4H, J = 4.8 Hz); 3.73 (apparent triplet, 4H, J = 4.6 Hz) IR (CH_2Cl_2): 1629 cm^{-1}. Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.77; H, 8.78. Found: C, 67.54; H, 8.72.

3-(4-morpholinyl)-2-cyclohexen-1-one (3b). Prepared by the method of Iida *et al.*[5a] from 4.13 g (36.8 mmol, 1.0 equiv.) of 1,3-cyclohexanedione and 3.6 mL (41 mmol, 1.1 equiv.) of morpholine in 50 mL of toluene. The title compound was isolated by Kugelrohr distillation (120-130 °C, 0.1 mm Hg) giving 5.39 g (85.1 %) of the desired product as a yellow solid, m.p. 87-91 °C. ^{1}H NMR ($CDCl_3$) δ: 1.94 (pentet, 2H, J = 6.4 Hz); 2.23 (t, 2H, J = 6.9 Hz); 2.36 (t, 2H, J = 6.3 Hz); 3.24 (t, 4H, J = 4.8 Hz); 3.68 (t, 4H, J = 5.1 Hz); 5.20 (s, 1H). Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34. Found: C, 66.07; H, 8.23.

2-Methyl-3-(4-morpholinyl)-2-cyclopenten-1-one (7). Prepared by the method of Iida *et al.*[5a] from 1.00 g (8.92 mmol, 1.0 equiv.) of 2-methyl-1,3-cyclopentanedione and 0.90 mL (10 mmol, 1.16 equiv.) of morpholine in 40 mL of toluene. The title compound was isolated by Kugelrohr distillation (110-116 °C, 0.07 mm Hg) giving 1.25 g (76.5 %) of the desired product as a yellow solid, m.p. 85-86 °C. ^{1}H NMR

($CDCl_3$) δ: 1.80 (s, 3H); 2.28-2.31 (m, 2H); 2.43-2.47 (m, 2H); 3.56 (apparent t, 4H, J = 5.7 Hz); 3.70 (apparent t, 4H, J = 5.1 Hz). ^{13}C NMR / DEPT ($CDCl_3$) **C:** δ: 106.9, 170.3, 202.9; **CH_2:** δ: 25.9, 31.5, 47.2, 65.8; **CH_3:** δ: 9.4. Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34. Found: C, 66.40; H, 8.51.

Grignard Addition to Enaminones: General Procedure.

The enaminone (0.5 to 1 mmol) was weighed into an oven-dried r.b. flask and dissolved in dry dichloromethane (four times the volume of ethereal Grignard reagent) under N_2. The solution was cooled with an ice-water bath and a solution (1.5-3.0M) of the Grignard reagent (3 equiv.) in diethyl ether was added dropwise using a syringe. The ice bath was removed and the reaction stirred at rt overnight.

The above solution was added to ~ 50 mL wet diethyl ether in a separatory funnel, then 1N HCl was added in ~1 mL portions until the pH was ~6, then ~ 20 mL of a 2N solution of NaOH in 80%-saturated aqueous NaCl was added and the phases were separated. The aqueous phase was extracted with two 25 mL portions of diethyl ether and the combined organic extracts were dried with sodium sulfate. Removal of ether by rotary evaporation gave the crude product which was chromatographed on silica gel (230/400 mesh) which had been deactivated by the addition of triethylamine (1 mL per 10 g silica gel) to the silica gel slurry prior to packing. Elution of the column with the appropriate mixture of hexanes and ether resulted in recovery of the *bis*-adduct followed by the substituted 3-alkylcyclohexenone. The aminocyclohexenes described below were prepared in this manner. The 3-alkylcyclohexenones[6,7] and 3-alkylcyclopentenones[8] produced in these reactions have been described elsewhere.

In reactions involving prior evaporation of ether, the Grignard reagent was added to a r.b. flask fitted with a septum and a stirring bar. A stream of nitrogen gas was passed through the flask, venting through a second syringe needle, until the Grignard reagent appeared as a gummy residue. The Grignard reagent was then suspended in dichloroamethane and the evaporation process repeated and placed under vacuum (~ 0.5 mm Hg) for 15 min. The Grignard reagent was then suspended in dichloromethane (4 mL per mmol RMgX), cooled with an ice-water slush bath, and a solution of the substrate enaminone in dichloromethane (1.5 mL per mmol enaminone) was added *via* syringe. The reaction was then allowed to warm to rt and stirred before being worked up as described above.

1,3-Dibutyl-2-methyl-1-(1-pyrrolidinyl)-2-cyclohexene (5b). ^1H NMR ($CDCl_3$) δ: 0.87 (t, 3H, J = 7.4 Hz); 0.90 (t, 3H, J = 6.9 Hz); 1.1 - 1.8 (m, 18H); 1.60 (s, 3H); 1.86 (m, 2H); 2.00 (t, 2H, J = 7.0 Hz); 2.48 (m, 2H); 2.57 (m, 2H). ^{13}C NMR / DEPT ($CDCl_3$) **C:** δ: 59.4, 129.9, 135.2; **CH_2:** δ: 21.9, 22.9, 23.7, 23.8, 26.3, 27.7, 30.1, 30.2, 34.4, 40.7, 45.6; **CH_3:** δ: 12.6, 14.1, 14.2. IR (film): 2970, 2960, 2925, 1455, 1370 cm^{-1}. Anal. Calcd for $C_{19}H_{35}N$: C, 82.24; H, 12.71. Found: C, 82.16; H, 12.53.

1,3-Diethyl-2-methyl-1-(1-pyrrolidinyl)-2-cyclohexene (5c). ^{1}H NMR ($CDCl_3$) δ: 0.73 (t, 3H, *J* = 7.5 Hz); 0.94 (t, 3H, *J* = 7.5 Hz); 1.3 - 1.8 (m, 10H); 1.61 (br s, 3H); 1.85 - 1.90 (m, 2H); 2.02 (br q, 2H, *J* = 7.5 Hz); 2,44 - 2.51 (m, 2H); 2.56 - 2.60 (m, 2H). ^{13}C NMR / DEPT ($CDCl_3$) **C:** δ: 59.6, 128.9, 136.9; **CH_2:** δ: 22.0, 23.8, 25.7, 27.6, 29.7, 32.9, 45.6; **CH_3:** δ: 9.9, 12.2, 12.3. IR (film): 2975, 2955, 2925, 1455, 1370, 1195, 1020 cm^{-1}. Anal. Calcd for $C_{15}H_{27}N$: C, 81.38; H, 12.29. Found: C, 81.15; H, 12.10.

1,3-Dibutyl-1-(1-pyrrolidinyl)-2-cyclohexene (5d). ^{1}H NMR ($CDCl_3$) δ: 0.89 (t, 6H, *J* = 6.6 Hz); 1.1 - 1.9 (m, 20H); (t 1.96 (t, 2H, *J* = 7.6 Hz); 2.55 - 2.60 (m, 4H); 5.27 (s, 1H) ^{13}C NMR / DEPT ($CDCl_3$) **C:** δ: 57.2, 139.3; **CH:** δ: 126.1; **CH_2:** δ: 20.8, 22.3, 23.6, 23.9, 26.1, 28.1, 28.5, 29.9, 37.7, 39.7, 45.6; **CH_3:** δ: 13.99, 14.09. IR (film): 2940, 2920, 2820, 1450, 1110 cm^{-1}. Anal. Calcd for $C_{18}H_{33}N$: C, 82.06; H, 12.63. Found: C, 81.82; H, 12.75.

1,3-Dibutyl-2-methyl-1-diethylamino-2-cyclohexene (5f). ^{1}H NMR ($CDCl_3$) δ: 0.87 (t, 3H, *J* = 7.3 Hz); 0.91 (t, 3H *J* = 7.1 Hz); 0.99 (t, 6H, *J* = 7.1 Hz); 1.0-1.1 (m, 2H); 1.15-1.60 (m, 11H); 1.58 (t, 3H, *J* = 1.7 Hz); 1.7-1.8 (m, 1H); 1.8-1.9 (m, 2H); 1.95-2.05 (m, 2H); 2.45 (apparent sextet , 2H, *J* = 7.2, 13.5 Hz); 2.53 (apparent sextet, 2H, *J* = 7.0, 13.5 Hz). ^{13}C NMR / DEPT ($CDCl_3$) **C:** δ: 63.5, 130.3, 135.4; **CH_2:** δ: 21.5, 23.0, 23.9, 28.0, 28.9, 30.1, 30.3, 34.5, 40.0, 44.6; **CH_3:** δ: 12.5, 14.1, 14.2, 17.8. Anal. Calcd for $C_{19}H_{37}N$: C, 81.65; H, 13.34. Found: C, 81.50; H, 13.12.

1,3-Dibutyl-2-methyl-1-(4-morpholinyl)-2-cyclohexene (5h). ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, 3H, *J* = 7.3 Hz); 0.90 (t, 3H, *J* = 7.2 Hz); 1.00 - 1.15 (m, 2H); 1.15 - 1.50 (m, 16H); 1.57 (s, 3H); 2.39 - 2.46 (m, 5 lines, 2H); 2.51 - 2.62 (m ,5 lines, 2H); 3.63 (t, 4H, *J* = 5.7 Hz). ^{13}C NMR / DEPT ($CDCl_3$) **C:** δ: 61.4, 128.4, 137.1; **CH_2:** δ: 21.3, 23.0, 23.7, 26.5, 27.7, 29.7, 30.1, 34.4, 39.1, 47.2, 68.3; **CH_3:** δ: 12.2, 14.1, 14.2. IR (film): 2940, 2920, 2820, 1450, 1110 cm^{-1}. Anal. Calcd for $C_{19}H_{35}NO$: C, 77.76; H, 12.02. Found: C, 77.90; H, 12.18.

1,3-Dibutyl-1-(4-morpholinyl)-2-cyclohexene (5j). ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, 6H, *J* = 7.3 Hz); 1.2 - 1.8 (m, 16H); 1.96 (t, 2H, *J* = 7.6 Hz); 2.47 - 2.51 (m, 4H); 3.66 (t, 4H, *J* = 4.4 Hz); 5.16 (s, 1H). ^{13}C NMR / DEPT ($CDCl_3$) **C:** δ: 58.4, 139.7; **CH:** δ: 126.9; **CH_2:** δ: 20.6, 22.3, 23.4, 25.4, 26.9, 28.3, 29.8, 37.7, 38.1, 46.3, 68.0; **CH_3:** δ: 13.9, 14.1. IR (film): 2940, 2920, 2820, 1450, 1110 cm^{-1}. Anal. Calcd for $C_{18}H_{33}NO$: C, 77.36; H, 11.90. Found: C, 77.29; H, 11.75.

1,3-Dibutyl-2-methyl-1-(1-pyrrolidinyl)-2-cyclopentene (9a). ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, 3H, *J* = 7.3 Hz); 0.92 (t, 3H, *J* = 6.8 Hz); 0.9-1.9 (m, 18H); 1.44 (s, 3H); 1.95 (t, 2H, *J* = 7.3 Hz); 2.3-2.4 (m, 2H); 2.5-2.6 (m, 2H). ^{13}C NMR / DEPT ($CDCl_3$) **C:** δ: 75.9, 133.9, 137.7; **CH_2:** δ: 22.6, 23.5, 23.8, 24.4, 26.4, 28.4, 30.1, 33.9, 38.8, 46.6; **CH_3:** δ: 10.4, 14.0, 14.2. Anal. Calcd for $C_{18}H_{33}N$: C, 82.11; H, 12.63. Found: C, 81.88; H, 12.49.

1,3-Dibutyl-2-methyl-1-(1-morpholinyl)-2-cyclopentene (9c). ^{1}H NMR ($CDCl_3$) δ: 0.87 (t, 3H, J = 7.3 Hz); 0.89 (t, 3H, J = 7.3 Hz); 1.1-1.4 (m, 14H); 1.42 (s, 3H); 1.8-2.0 (m, 2H); 2.3-2.4 (m, 2H); 2.5-2.6 (m, 2H); 3.66 (t, 4H, J = 4.4 Hz). ^{13}C NMR / DEPT ($CDCl_3$) **C:** δ: 76.7, 132.3, 139.0; **CH_2:** δ: 22.6, 23.4, 23.7, 26.5, 28.3, 30.0, 33.9, 36.8, 46.6, 67.7; **CH_3:** δ: 9.95, 13.89, 14.07. Anal. Calcd for $C_{18}H_{33}NO$: C, 77.36; H, 11.90. Found: C, 77.29; H, 11.69.

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