

**PREPARATION AND CONFORMATIONAL ANALYSIS OF SEVERELY HINDERED β -DIKETONES.
DIPOLE MOMENT DETERMINATIONS AND THEORETICAL CALCULATIONS.**

M. MORENO-MAÑAS*, A. GONZÁLEZ, C. JAIME,¹ M.E. LLORIS, J. MARQUET,
A. MARTÍNEZ, A.C. SIANI, A. VALLRIBERA

Department of Chemistry. Universitat Autònoma de Barcelona.
Bellaterra. 08193-Barcelona. Spain.

I. HERNÁNDEZ-FUENTES, M.F. REY-STOLLE, C. SALOM

Departamento de Química Física I. Facultad de Ciencias Químicas.
Universidad Complutense. 28040-Madrid. Spain.

(Received in UK 8 May 1991)

Key words: β -Diketones; Preparation from Co(II) complexes;
Conformational analysis; Dipole moments; Molecular Mechanics

Abstract.- Several β -diketones bearing bulky substituents at the intercarbonyl positions have been prepared by alkylation of the cobalt(II) complexes of the unsubstituted diketones. Agreement between experimental and calculated dipole moments is fairly good thus rendering Molecular Mechanics a safe tool for the conformational analysis of the title molecules. The most populated conformations have been evaluated for nine β -diketones bearing 1- and 2- adamantyl, *tert*-butyl, cyclohexyl, 1-phenylethyl and benzhydryl groups as well as two methyl groups and one methyl plus one 1-adamantyl groups.

INTRODUCTION. Conformational analysis of open-chain compounds is limited by their inherent conformational complexity. The advent of Molecular Mechanics (MM)² has opened new possibilities in this field. Calculations alone are not sufficient, however, and, if possible, cross checking with experimental data (NMR methods or others) is highly desirable.

In a preliminary communication³ we reported the useful combination of MM and dipole moment determinations to evaluate the conformational preferences of 3-(1-adamantyl)pentane-2,4-dione (1) and 4-(1-adamantyl)-2,2,6,6-tetramethylheptane-3,5-dione (2). Since then, the combination of dipole moment determinations and theoretical calculations of different degrees of complexity has become quite popular.⁴ The idea is not new, however. Thus, in 1978 Allinger and coworkers studied the conformations of 3,3-dimethylpentane-2,4-dione (8) by a combination of dipole moments and MM.⁵

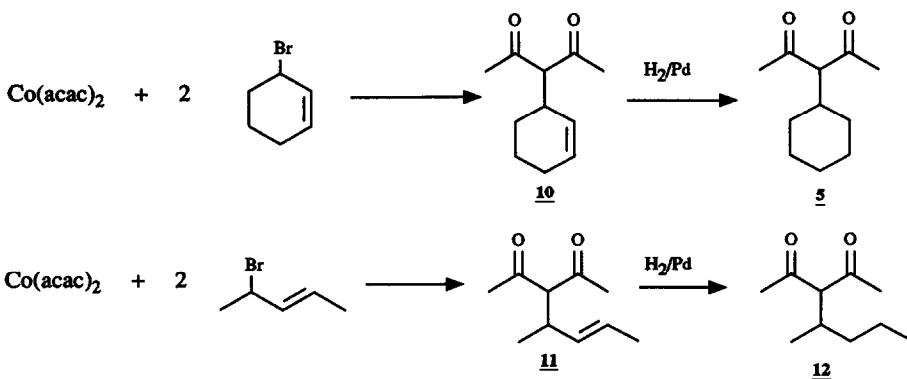
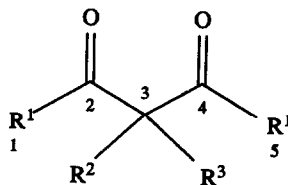
We now want to present an extension of our work to several β -diketones bearing secondary and tertiary substituents at the intercarbonyl position as well as to some disubstituted β -diketones. All the compounds studied exist only in the diketo forms, no keto-enol tautomers being detected by NMR analysis.

PREPARATION OF COMPOUNDS. The studied compounds are: 1, 2, 3-(2-adamantyl)pentane-2,4-dione (3), 3-*tert*-butylpentane-2,4-dione (4), 3-cyclohexylpentane-2,4-dione (5), 3-(1-phenylethyl)pentane-2,4-dione (6), 3-benzhydrylpentane-2,4-dione (7), 8, and 3-(1-adamantyl)-3-methylpentane-2,4-dione (9).

Compounds 1-7 were prepared by alkylation of the cobalt(II) complexes of the unsubstituted diketones with the corresponding alkyl halides. Compounds 16a, 26a, 66b and 76b have been previously described by us. Compound 9 was prepared by a similar alkylation of the copper(II) complex of 3-methylpentane-2,4-dione.⁷ The disubstituted diketone 8 was prepared by conventional methods.⁵

Our method of alkylation has proved useful for the preparation of diketones 3 and 4 bearing a secondary or a tertiary substituent. Other secondary substituents could not be introduced directly, probably because free radicals are intermediates in the cobalt (and copper) method⁸ and secondary free radicals do not form easily. Compound 5 was, however, prepared by cobalt-mediated alkylation with 3-bromocyclohexene to afford 3-(2-cyclohexen-1-yl)pentane-2,4-dione (10), which gave 5 upon hydrogenation under palladium on charcoal catalysis. This method is useful for the introduction of secondary radicals at the intercarbonyl position, as evidenced by a similar sequence leading to 3-acetyl-4-methyl-5-hepten-2-one (11) and 3-acetyl-4-methyl-2-heptanone (12).

Compound	R ¹	R ²	R ³
1	Me	1-Adamantyl	H
2	<i>t</i> -Bu	1-Adamantyl	H
3	Me	2-Adamantyl	H
4	Me	<i>t</i> -Bu	H
5	Me	Cyclohexyl	H
6	Me	1-Phenylethyl	H
7	Me	Benzhydryl	H
8	Me	Me	Me
9	Me	1-Adamantyl	Me



DIPOLE MOMENTS. Dipole moments were determined by the Debye method, in cyclohexane for all compounds and also in benzene for compounds 1 and 2. Two different approximations were followed in the evaluation of the experimental values: the Guggenheim-Smith method⁹ and the Halverstadt-Kumler method.¹⁰ In the latter case the contribution of the atomic polarization was considered to be 5% and 15% of the electronic polarization. As can be seen from Table 1 the three approaches showed no significant differences.

THEORETICAL CALCULATIONS. An MM2 analysis was undertaken for compounds 1-9. Allinger's MM2(77) force field^{11,12} together with all MM2(85) parameters¹³ were used through this work.

One torsional energy surface was calculated for each product. The rotation of all other bonds producing non-equivalent conformers was undertaken by the one-bond drive technique on each previously obtained minimum. Torsional energy surfaces were obtained driving both R-CO-C-CO (R = Me or tert-Bu) dihedral angles (ω_1 and ω_2) present in every molecule from -180° to $+180^\circ$ in 15° steps. In the one-bond drive rotations, 10° steps were used for all bonds.

All the conformers obtained by MM2 calculations were used as starting conformations to be optimized by the MOPAC program¹⁴ under the MNDO approach.¹⁵ Finally, a set of dipole moments was computed by using the formula for the bulk dipole moments: $\mu = (\sum n_i \mu_i^2)^{1/2}$. The individual μ_i and n_i for each conformer were evaluated as follows:

a) With the MM2 program using three different dielectric constants: 1.5 (vacuum value routinely used in MM2 calculations), 2.02 (cyclohexane) and 2.28 (benzene). The final bulk dipole moments so calculated are gathered in columns 1, 2 and 3 of Table 1.

b) With the MNDO program with one single self consistence field (1SCF) and with full optimization. The calculated bulk dipole moments are in columns 5 and 6.

c) By mixing the molar fractions obtained by MM2 calculations with the individual dipole moments (μ_i) originated from the 1SCF calculations on the MNDO program over geometries from MM2. Column 4 of Table 1 contains the bulk dipole moments computed by this approach.

RESULTS AND DISCUSSION. Table 1 contains the calculated dipole moments for the six different approaches considered, as well as the ones determined experimentally by the methods of Guggenheim-Smith and Halverstadt-Kumler. The root mean square (rms) statistical criterion has been adopted to decide which is the best computational approach. Predictions by MM2 using a dielectric constant of 1.5 are the best (rms = 0.25). This rms value should be considered as fairly good, taking into account that all but one of the compounds studied have low dipole moments so that the relative errors in measurements can be high. The worst approach was that based on full optimization under the MNDO program (rms = 1.19). Our discussion will therefore be based on the data of column 1 (MM2 with a dielectric constant of 1.5).

It is interesting to note that dipole moments determined in cyclohexane (dielectric constant 2.02) are in better agreement with the MM2 calculations using the standard 1.5 value corresponding to vacuum. Our previous studies on compounds 1 and 2³ were made using older MM2 parameters.¹⁶ The calculated values for dipole moments with dielectric constants 2.02 and 2.28 were very close to the values determined in cyclohexane and benzene, respectively. The values calculated for dielectric constant 1.5 were not as close to the experimental figures. Nevertheless, we preferred to use the more modern parameters in the present study (MM2(85)).

TABLE 1. Calculated and experimental dipole moments for compounds 1-9

Compound	-----Calculated-----						-----Experimental-----		
	1(a)	2(b)	3(c)	4(d)	5(e)	6(f)	GS(g)	HK(h)	HK(i)
1	2.52	2.80	2.88	1.81	2.46	3.98	2.50 (2.86) ^(j)	2.46 (2.84) ^(j)	2.40 (2.79) ^(j)
2	4.06	4.78	4.95	2.73	3.71	3.91	4.18 (4.38) ^(j)	4.15 (4.36) ^(j)	4.09 (4.32) ^(j)
3	1.90	2.39	2.56	1.46	1.80	3.67	2.01	1.97	1.88
4	2.57	2.84	2.94	2.03	2.32	3.99	2.48	2.45	2.41
5	2.12	2.48	2.65	1.62	2.16	3.26	2.09	2.06	1.99
6	2.28	2.71	2.85	1.69	1.93	3.68	2.06	2.02	1.94
7	2.80	3.15	3.28	2.45	2.24	3.45	2.27	2.22	2.13
8	1.95	2.06	2.11	1.56	3.46	3.61	2.42	2.40	2.36
9	2.84	2.82	2.82	2.02	2.92	2.94	2.80	2.77	2.71
rms ^k	0.25	0.49	0.60	0.92	0.39	1.19			

^aMM2 program, dielectric constant 1.5; ^bMM2 program, dielectric constant 2.02; ^cMM2 program, dielectric constant 2.28. ^dMixing the molar fractions obtained by MM2 calculations with the individual dipole moments originated from the 1SCF calculations on the MNDO program over geometries from MM2. ^eMNDO program with one single self consistent field (1SCF); ^fMNDO program with full optimization; ^gGuggenheim-Smith method; ^hHalverstadt-Kumler method, the contribution of the atomic polarization was considered to be 5% of the electronic polarization; ⁱHalverstadt-Kumler method, the contribution of the atomic polarization was considered to be 15% of the electronic polarization; ^jIn parentheses values determined in benzene; ^krms = $(\sum (\mu_{\text{calc}} - \mu_{\text{GS}})^2 / N)^{1/2}$.

The MM2 program has predicted sets of conformers corresponding to energy minima. All the conformers predicted can be grouped into pairs of enantiomers. In other words, no conformers possessing symmetry planes have been detected. Also no symmetry axes are present in the predicted conformers. This means that neither entropy of mixing correction ($+RT\ln 2$ for d,l pairs) nor corrections of entropy for symmetry ($-RT\ln s$, s being the order of the symmetry axis in one given conformer) need to be introduced.⁵ Entropy differences between conformers possessing the same symmetry (none in our predicted conformers) should be very small since in such situations the major contributions to entropy arise from groups of atoms.¹⁷ In other words, the differences in conformational energies calculated by MM2 can be considered equal to the differences in Gibbs free energies.

The conformational features for each conformation corresponding to a minimum have been described in terms of dihedral angles ω_1 (C1-C2-C3-C4) and ω_2 (C2-C3-C4-C5) and the angle between the two dipoles (α). In Table 2 one enantiomer of each pair is represented and the corresponding relative energies, population (overall for both enantiomers), ω_1 and ω_2 (for the enantiomer shown) and α (for both enantiomers) are given.

TABLE 2. Relative Energies (Kcal/mol), population (%), dihedral angles ω_1 (C1-C2-C3-C4) and ω_2 (C2-C3-C4-C5), angles between dipoles α ($^\circ$) and calculated dipole moments (D units) (MM2) for all conformers. Only one conformer of each enantiomeric pair is represented. The population refers to the contribution of both enantiomers

	1A	1B	1C	2A	2B	3A	3B	4A	4B	4C
Kcal/mol	0.00	0.30	0.34	0.00	0.09	0.00	1.14	0.00	0.31	0.34
%	46.03	27.89	26.03	53.66	46.34	87.08	12.78	46.43	27.41	26.12
ω_1	36.90	52.96	-54.60	-97.98	53.74	63.97	-107.65	36.30	50.97	-55.07
ω_2	78.32	63.74	114.59	133.22	81.30	76.48	65.09	80.64	68.91	116.66
α	168.77	172.80	46.27	28.54	169.63	168.85	30.27	168.74	174.56	47.45
μ	1.15	0.34	4.72	5.51	0.64	0.54	4.99	1.23	0.45	4.73
	5A	5B	6A	6B	6C	6D	7A	7B	8A	
Kcal/mol	0.00	1.19	0.00	0.10	0.76	0.93	0.00	0.40	0.00	
%	75.74	10.10	41.21	34.79	11.35	8.54	65.36	33.58	80.14	
ω_1	-64.03	112.32	-60.94	72.86	106.56	60.11	61.82	-59.68	-65.90	
ω_2	-77.49	-64.66	-72.69	65.98	-63.47	-109.91	69.06	111.67	-65.91	
α	167.68	34.08	174.12	170.56	31.43	36.86	177.41	39.26	174.40	
μ	0.60	5.00	0.52	0.25	4.86	4.87	0.30	4.76	0.21	
	9A	9B	9C							
Kcal/mol	0.00	0.02	0.30							
%	32.88	31.70	19.68							
ω_1	42.36	22.76	-128.30							
ω_2	56.42	86.93	29.57							
α	157.81	158.36	87.30							
μ	0.82	1.94	3.99							

From the above data some conclusions can be drawn, but before we go into greater detail it should be noted that all the measured dipole moments except two (compounds 2 and 9) are lower than or equal to the contribution of single a ketone carbonyl group (about 2.5D). This means that the preferred conformations (for all compounds except 2) are those in which minimization of dipole repulsion is attained. The discussion to follow will be presented for only one enantioisomer of each pair. Only conformers populated to a larger extent than 10% will be considered (5% of each enantioisomer). The geometric descriptions for all conformers discussed below are gathered in Table 2.

a) Compounds 1, 4 and 9

Compounds 1 and 4 possessing tertiary radicals at C3, exhibit very similar dipole moments (calculated and measured). The conformations predicted are practically the same for both compounds: A and B having low dipole moments accounting for 74% of the population and a third conformation (C), exhibiting a dipole moment much higher than 2.5D, accounting for 26% of the conformational mixture. From these data it could be concluded that the tert-butyl and the 1-adamantyl groups are equivalent from the conformational point of view.

Compound 9 presented more difficulties in the calculations possibly because the congestion of groups (two vicinal quaternary carbon atoms) reduces the mobility for the rotation around the sigma bonds. It presents a family of conformers (A,B) showing low dipole moments accounting for 65% of the total, in which the dipole repulsion is low as well as one conformer (C) accounting for 20% and exhibiting a high dipole moment. Thus, the conformational behaviour of 9 is similar to that of 1 and 4.

b) Compounds 3 and 5

These compounds bear a secondary group at the intercarbonyl position and their behaviour is similar. Both measured dipole moments are close to each other. Compound 5 has one stable conformer (A) which has a low dipole moment, accounting for 76% of the conformational mixture. The balance is made up of different conformations having high dipole moments. One of them (B) is populated to the extent of 10%. Diketone 3 exhibits similar behaviour: one low dipole moment conformer (A) represents 87% of the mixture, and a high dipole moment conformer (B) is present to the extent of 13%.

c) Compounds 6 and 7

Both present similar behaviour, but compound 7 has local symmetry around the substituent at C3. It exhibits two highly populated conformers. The low dipole moment conformer (A) accounts for 65% of the total and the high dipole moment one (B) is somehow less populated (34%). Since there is no local symmetry at the substituent at C3 in compound 6, the conformers are not enantioisomers but diastereoisomers. Two of them (A,B) representing 76% of the conformational mixture have low dipole moments, and correspond to conformer A in 7. The other two conformers (C,D) are populated to the extent of 20% and have high dipole moments.

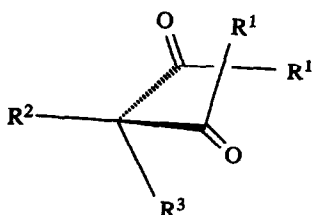
d) Compound 8

Only one conformer with a population above 5% is predicted for **8** and that is conformer (A) (80%). It exhibits a low dipole moment. Our calculated bulk dipole moment is much lower than that calculated in the earlier work by Allinger⁵ and much closer to the experimental value, a reflection of the improvement of the MM method since then.

e) Compound 2

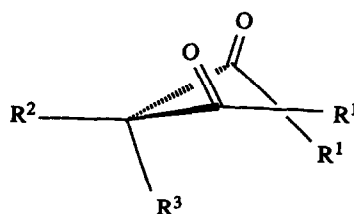
The conformational behaviour of **2** is different from those described above. Its determined and calculated dipole moments are much higher than 2.5D. The tendency, already visible in **1**, **4** and **9** is clear here. This molecule has very strong steric congestion and the best conformers are, therefore, those in which this is minimized at the expense of the dipole repulsion which is now of lesser importance. The most populated conformation is that having a high dipole moment (A, 54%), compared with the low dipole moment one (B) which accounts for only 46% of the conformational mixture.

In summary, there are basically two different types of conformers in diketones **1-9**: one has low dipole moments and the angle α ranges between 157 and 178°; the second has higher dipole moments and angles α between 28 and 88°. In the second type of conformations the groups at C1 and C5 (Me or t-Bu) are far from the bulkier substituent at C3. As indicated by the experimental dipole moments, the contribution of these conformers to the population increase with increasing bulk of the substituents at C3. Thus, $\mu = 2.01\text{D}$ and 2.09D for secondary radicals (compounds **3** and **5**) and 2.48D and 2.50D for tertiary radicals (compounds **4** and **1**). If additional strain is introduced at positions C1 and C5, as in compound **2** ($\mu = 4.18\text{D}$), conformations possessing a high degree of dipole-dipole repulsion can predominate.



Low Dipole Moment Conformers

1A, **1B**, **2B**, **3A**, **4A**, **4B**, **5A**, **6A**,
6B, **7A**, **8A**, **9A**, **9B**



High Dipole Moment Conformers

1C, **2A**, **3B**, **4C**, **5B**, **6C**, **6D**, **7B**, **9C**

EXPERIMENTAL

a) Dipole moments: the solvents used for calibrating the dielectric cell and for all the measurements (dielectric constant, specific volume and refractive index) were from Carlo Erba RPE and were dried before use over Merck 4Å molecular sieves. The dielectric measurements were performed on a WIW Model DK 06 Multidekometer, at a frequency of 2.0 MHz. The cell used was made of silvered Pyrex glass and was calibrated at the working temperature, 25.00 ± 0.02 °C using liquids of well known dielectric constants (i.e., benzene, toluene and cyclohexane).^{18,19} The differences in refractive index of solutions and solvent were measured at 546 nm in a Brice Phoenix 2000V differential refractometer, calibrated with aqueous KCl. For specific volume determinations an Anton Paar DMA 55 digital densimeter was used, with distilled water and air as calibrating substances. The temperature in the measuring cell was regulated to 25.00 ± 0.01 °C.

a) Preparation of compounds 3, 4, 5 and 123-(2-Adamantyl)pentane-2,4-dione, 3.

A mixture of 2-bromoadamantane (1.075 g, 5.0 mmole) and $\text{Co}(\text{acac})_2$ (0.645 g, 2.5 mmole) in 1,1,2,2-tetrachloroethane (1.5 ml) was heated at 185°C for 90 minutes in a closed reactor. The mixture was partitioned between dichloromethane and 10% HCl. The organic layer was washed, dried and evaporated. The residue was treated overnight with active charcoal in chloroform at room temperature. The mixture was filtered and the solvent evaporated. The residue was chromatographed through silica gel with mixtures of hexane-ethyl acetate to give recovered 2-bromoadamantane, traces of 2-acetonyladamantane, 2-adamantyl acetate (190 mg) and 3 (270 mg, 21 %); m.p. 76-77.5°C (ether-petroleum ether); IR(KBr): 1694 cm^{-1} ; PMR(CDCl_3): δ 1.43-1.90 (m, 14H), 2.18 (s, 6H), 2.63 (broad d, J 12.2 Hz, 1H), 4.24 (d, J 12.2 Hz, 1H); MS: m/e 234(M, 2), 43(100).

Calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_2$: C, 76.88; H, 9.46. Found: C, 76.55; H, 9.46.

3-t-Butylpentane-2,4-dione, 4.

A mixture of $\text{Co}(\text{acac})_2$ (1.29 g, 5 mmole), t-butyl iodide (1.85 g, 10 mmol) and chloroform (2 ml) was heated at 100°C for 4 h in a closed reactor. The mixture was partitioned between dichloromethane and 10% HCl. The organic layer was washed with water and eventually with aqueous sodium thiosulfate, dried and evaporated. The residue was taken up in chloroform and treated overnight with activated charcoal. The mixture was filtered and the solvent evaporated to give 236 mg (15%) of diketone 4 as an oil; bp 35°C (oven temperature)/0.01 mmHg; IR(film): 1721, 1697 cm^{-1} ; PMR(CDCl_3): δ 1.08(s, 9H), 2.20(s, 6H), 3.65(s, 1H), these data are coincident with those previously reported;²⁰ MS: m/e 157(M+1, 11), 48(23), 47(22), 43(100).

3-(2-Cyclohexen-1-yl)pentane-2,4-dione, 10.

A mixture of $\text{Co}(\text{acac})_2$ (12.90 g, 0.05 mole) and 3-bromocyclohexene (9.73 g, 0.06 mole) in chloroform (20 ml) was heated at 100°C for 4 hours in a closed reactor. After cooling, the mixture was partitioned between hexane and 10% hydrochloric acid. The

organic layer was washed, dried and evaporated to afford a residue which was taken into chloroform and treated with activated charcoal overnight. The mixture was filtered, the solvent evaporated and the residue distilled (bp 97°C/0.02 mmHg) to give **10** (6.74 g 75%); IR(film): 1723, 1699 cm^{-1} ; PMR(CDCl_3): δ 1.12-2.17 (m, 6H), 2.22 (s, 6H), 2.81-3.23 (m, 1H), 3.61 (d, J 10.3 Hz, 1H), 5.35 (long range coupled d, J 9.3 Hz, 1H), 5.78 (m, 1H); CMR(CDCl_3): δ 20.4, 24.7, 26.4, 29.4, 29.8, 35.4, 74.5, 127.0, 129.7, 203.3, 203.6; MS: m/e 180(M, 1), 137(55), 43(100).

3-Cyclohexylpentane-2,4-dione, 5.

A mixture of **10** (315 mg, 1.75 mmole) and a catalytic amount of 10% Pd/C in ethanol (25 ml) was shaken with hydrogen at atmospheric pressure. After 2 hours the mixture was filtered and the solvent evaporated to afford 250 mg (79%) of **5**; m.p. 47-8°C (petroleum ether); IR(KBr): 1727, 1694 cm^{-1} ; PMR(CDCl_3): δ 1.10-1.80 (m, 11H), 2.16 (s, 6H), 3.50 (d, J = 10.9 Hz, 1H); MS: m/e 183(M+1, 17), 101(52), 97(24), 43(100).

Calcd. for $\text{C}_{11}\text{H}_{18}\text{O}_2$: C, 72.49; H, 9.96. Found: C, 72.39; H, 10.12.

3-Acetyl-4-methyl-5-hepten-2-one, 11.

A mixture of 4-bromo-2-pentene (prepared according to Ref. 21) (1.60 g, 0.011 mole), $\text{Co}(\text{acac})_2$ (1.38 g, 0.005 mole) and chloroform (2 ml) was heated at 100°C for 2 hours in a closed reactor. The colour changed from pink to green. The mixture was partitioned between chloroform and 1N HCl. The organic layer was dried and evaporated to afford a residue (2 g, nearly 100% yield) of spectroscopically pure **11** which was distilled (40-5°C/0.5 mmHg) to afford pure **11** (58%); IR(film): 1723, 1699, 970 cm^{-1} ; PMR(CDCl_3): δ 0.98(d, J 7.7 Hz, 3H), 1.63 (d, J 5.1 Hz, 3H), 2.12 (s, 3H), 2.20 (s, 3H), 2.80-3.22 (m, 1H), 3.56 (d, J 10.3 Hz, 1H), 5.06-5.77 (m, 2H); CMR(CDCl_3): δ 17.61, 18.77, 29.34, 29.84, 37.42, 75.60, 126.14, 132.31, 203.56; MS: m/e 43(100); MS (chemical ionization): m/e 186(M + 18, 13).

Calcd. for $\text{C}_{10}\text{H}_{16}\text{O}_2$: C, 71.39; H, 9.59. Found: C, 71.49; H, 9.83.

3-Acetyl-4-methyl-2-heptanone, 12.

A mixture of **11** (0.50 g, 2.9 mmole) and 10% Palladium on charcoal (0.05 g) in absolute ethanol (25 ml) was shaken in hydrogen at atmospheric pressure. After 3 hours the mixture was filtered through celite and the solvent evaporated to afford 0.38g (78%) of **12** which was distilled (50°C/0.07 mmHg). The distilled compound (0.26 g, 53%) presented IR(film): 1722, 1698 cm^{-1} ; PMR(CDCl_3): δ 0.6-1.9 (m, 10H), 2.2 (s, 6H), 3.60 (d, J 10.7 Hz, 1H); CMR(CDCl_3): δ 13.94, 16.88, 19.65, 29.55, 29.61, 33.54, 36.68, 76.48, 204.31, 204.36.

Calcd. for $\text{C}_{10}\text{H}_{18}\text{O}_2$: C, 70.55; H, 10.66. Found: C, 70.36; H, 10.95.

ACKNOWLEDGEMENTS

Financial support from DGICYT through project PB87-0030 is gratefully acknowledged. We are also indebted to "Conselho Nacional de Pesquisa" (Brazil) for a postdoctoral scholarship to one of us (A.C. Siani).

REFERENCES AND FOOTNOTES

- 1.- To whom correspondence concerning calculations should be addressed
- 2.- Burkert, U.; Allinger, N.L. "Molecular Mechanics". ACS Monograph 177; Washington, D.C., 1982.
- 3.- Moreno-Mañas, M.; González, A.; Jaime, C.; Marquet, J.; Hernández-Fuentes, I.; Salom, C.; Bellanato, J. J. Chem. Soc., Chem. Commun. **1987**, 1706.
- 4.- a) Saiz, E.; Horta, A.; Gargallo, L.; Hernández-Fuentes, I.; Abradelo, C.; Radic, D. J. Chem. Res. (S) **1988**, 280; b) Hernández-Fuentes, I.; Abradelo, C.; Domínguez, C.; Csáky, A.G.; Plumet, J.; Cativiela, C.; Mayoral, A.; Gaset, A.; Rigal, L. Heterocycles **1989**, 29, 657; c) Herrero, A.; Ochoa, C.; Stud, M.; Florencio, F.; Hernández-Fuentes, I.; Abradelo, C.; De Paz, J.L.C. J. Org. Chem. **1989**, 54, 5025; d) Claramunt, R.M.; Elguero, J.; Fabre, M.J.; Foces-Foces, C.; Hernández-Cano, F.; Hernández-Fuentes, I.; Jaime C.; López, C. Tetrahedron **1989**, 45, 7805; e) Lumbroso, H.; Bertin, D.M.; Olivato, P.R.; Bonfada, E.; Mondino, M.G.; Hase, Y. J. Mol. Struct. **1989**, 212, 113.
- 5.- Allinger, N.L.; Dosen-Mićović, L.; Viskocil, Jr., J.F.; Thomas Tribble, M. Tetrahedron **1978**, 34, 3395.
- 6.- a) González, A.; Marquet, J.; Moreno-Mañas, M. Tetrahedron **1986**, 42, 4253; b) Marquet, J.; Moreno-Mañas, M. Synthesis **1979**, 348.
- 7.- Lloris, M.E.; Marquet, J.; Moreno-Mañas, M. Tetrahedron Lett. **1990**, 31, 7489.
- 8.- Marquet, J.; Moreno-Mañas, M.; Pacheco, P.; Vallribera, A. Tetrahedron Lett. **1988**, 29, 1465.
- 9.- a) Guggenheim, E.A. Trans. Faraday Soc. **1949**, 45, 714; b) Guggenheim, E.A. Trans. Faraday Soc. **1951**, 47, 573; c) Smith, J.W. Trans. Faraday Soc. **1950**, 46, 394.
- 10.- Halverstadt, I.F.; Kumler, W.D. J. Am. Chem. Soc. **1942**, 64, 2988.
- 11.- Allinger, N.L.; Yuh, Y. Quantum Chemistry Program Exchange **1980**, 12, 395.
- 12.- Allinger, N.L. J. Am. Chem. Soc. **1977**, 99, 8127.
- 13.- MM2(85) Parameters; Allinger, N.L., personal communication.
- 14.- Stewart, J.J.P. Quantum Chemistry Program Exchange **1987**, 455.
- 15.- Dewar, M.J.S.; Thiel, W. J. Am. Chem. Soc. **1977**, 99, 1977.
- 16.- Original MM2(77) parameters: Ref. 11.
- 17.- Benson, S.W.; Cruickshank, F.R.; Golden, D.M.; Haugen, G.R.; O'Neal, H.E.; Rodgers, A.S.; Shaw, R.; Walsh, R. Chem.Rev. **1969**, 69, 279.
- 18.- Petro, A.J.; Smith, G.P. J. Am. Chem. Soc. **1957**, 79, 6142.
- 19.- Heston, W.M.; Smith, G.P. J. Am. Chem. Soc. **1950**, 72, 92.
- 20.- Boldt, P.; Miltzer, H. Tetrahedron Lett. **1966**, 3599.
- 21.- Mulliken, S.P.; J. Am. Chem. Soc. **1935**, 57, 1605.