# Carbon-13 NMR Spectra of Octahydro-1,4-naphthoquinones and of Their Derivatives

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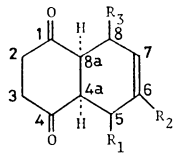
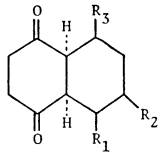
The $^{13}C$ NMR spectra are reported for hexahydro- and octahydro-1,4-naphthoquinones and their derivatives. The shielding trends of the methyl group are utilized for conformational analysis. A comparison of octahydro-1,4-naphthoquinones with the corresponding decalins reveals that the effects of the carbonyl group are the large downfield shift of the $\alpha$-carbons and the upfield shifts of the $\beta$- and $\gamma$-carbons.

$^{13}C$ NMR spectroscopy is a powerful method for clarifying stereochemical problems. Systematic studies of methyldecalins and decahydroquinolines have provided useful parameters for signal assignments.[1,2] This paper deals with a $^{13}C$ NMR study of *cis*-2,3,4a,5,8,8a-hexahydro- and *cis*-octahydro-1,4-naphthoquinones (**1a,b—5a,b**), *trans*-octahydro-1,4-naphthoquinones (**1c—3c**), and a number of derivatives (**6a,b, 7—13, 14a,b**).

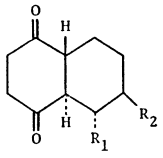
Natural-abundance 15.04 MHz $^{13}C$ FT-NMR spectra were obtained by use of the $^1H$ noise-decoupling technique. The signals of methyl, methylene, and methine carbons were identified by a combination of off-resonance decoupling and partially relaxed FT spectra.[3]



1a—5a

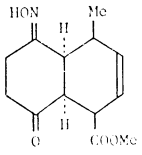


1b—5b

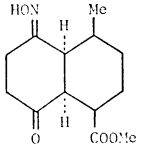


1c $R_1,R_2$=H
2c $R_1$=Me $R_2$=H
3c $R_1$=H $R_2$=Me

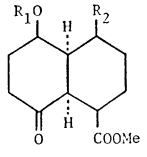
1a,b $R_1,R_2,R_3$=H
2a,b $R_1$=Me $R_2,R_3$=H
3a,b $R_2$=Me $R_1,R_3$=H
4a,b $R_1$=COOMe $R_2,R_3$=H
5a,b $R_1$=COOMe $R_2$=H $R_3$=Me



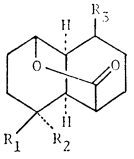
6a



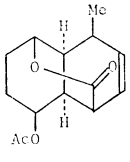
6b



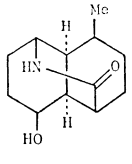
7 $R_1,R_2$=H
8 $R_1$=H $R_2$=Me
9 $R_1$=Ac $R_2$=H
10 $R_1$=Ac $R_2$=Me



11 $R_1,R_2$=O $R_3$=H
12 $R_1,R_2$=O $R_3$=Me
13 $R_1$=OH $R_2$=H $R_3$=Me
14b $R_1$=OAc $R_2$=H $R_3$=Me



14a



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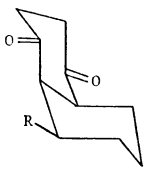
## Results and Discussion

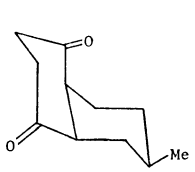
*Materials.* Compounds **1a—5a** were prepared from the Diels-Alder adduct[4-8] of *p*-benzoquinone and the corresponding diene by zinc reduction, respectively. Catalytic hydrogenation of **1a—5a** provided **1b—5b**, respectively.[4,8,9] The configuration of the methyl group in **3b** was estimated to be *cis-syn* because of the hydrogenation from less hindered side. Compound **2b** was isomerized into *trans*-**2c** by acid treatment and **3b** into *trans*-**3c** by alumina column. Hydrogenation of **6a**, derived from **5a**, with platinum oxide in methanol provided the dihydro keto oxime (**6b**), whereas that in acetic acid afforded the $\delta$-lactam (**15**). The $^{13}C$ NMR spectrum of **15** was similar to that of **13** except for C-1, supporting the position of the hydroxyimino group and the cis ring junctions in **6a** and **6b**. Compounds **10** and **14b** were obtained by acetylation of **8** and **13**, respectively.[8]

The chemical shifts of the $\Delta^{6,7}$-compounds (**1a—6a, 14a**) are summarized in Table 1, those of the octahydro-compounds (**1b—6b, 1c—3c**) in Table 2, and those of **7—13** and **14b** in Table 3.

*Signal Assignments.* Assignments for the signals in **2b, 3b,** and **4b** were made on their preferred conformations shown below. The methylene signal at 26.62 ppm in **4b** was assigned to C-8, since it was shifted upfield upon reduction of the C-1 carbonyl to the hydroxyl group (to **7**). Accordingly, the signal at 26.01 ppm in **2b** was assigned to C-8, which seems to be little affected by the substituent. Carbons $\alpha$ to the double bond in cyclohexenes are characteristically shielded ($\Delta\delta=\delta_C^{alkane}-\delta_C^{alkene}>0$).[10] The shielding trends of the double bonds for C-5 in **2a** and **4a** ($\Delta\delta$ 2.23 ppm between **2a** and **2b**; $\Delta\delta$ 1.22 ppm between **4a** and **4b**) support the assignments for C-8 in **2b** and **4b** ($\Delta\delta$ 3.45 ppm between **2a** and **2b**; $\Delta\delta$ 2.80 ppm between **4a** and **4b**). Saturation of the double bonds in **1a—6a** causes the downfield shifts of C-4a and -8a. The trend is in agreement with the



2b R=Me
4b R=COOMe



3b

Table 1. $^{13}C$ NMR chemical shifts of the $\Delta^{6,7}$-compounds[a)]

| Compound | **1a** | **2a** | **3a** | **4a** | **5a** | **6a**[b)] | **14a**[c)] |
|---|---|---|---|---|---|---|---|
| C-1 | 209.24 | 209.96* | 208.83* | 208.75* | 207.85* | 155.38 | 75.07 |
| C-2 | 35.79 | 35.34 | 35.95 | 35.18 | 34.73 | 26.09 | 30.31 |
| C-3 | 35.79 | 37.13 | 35.95 | 36.32 | 37.61 | 35.87 | 22.07 |
| C-4 | 209.24 | 209.64* | 209.15* | 207.04* | 210.29* | 209.48 | 72.35 |
| C-4a | 44.76 | 48.69 | 45.53** | 46.62 | 46.05 | 45.08 | 39.60 |
| C-5 | 23.49 | 30.96 | 28.20 | 40.01 | 39.44 | 38.26* | 37.17* |
| C-6 | 124.42 | 130.95 | 131.72 | 125.03 | 121.37 | 121.42 | 125.35 |
| C-7 | 124.42 | 122.95 | 118.41 | 123.20 | 131.27 | 130.71 | 135.90 |
| C-8 | 23.49 | 22.56 | 24.06 | 23.82 | 30.55 | 28.08 | 34.77 |
| C-8a | 44.76 | 45.20 | 44.84** | 45.00 | 48.33 | 37.65* | 37.78* |
| C-Me | | 17.65 | 23.37 | | 17.40 | 17.40 | 16.51 |
| COO | | | | 171.98 | 172.06 | 171.98 | 171.98 |
| O-Me | | | | 52.10 | 52.10 | 51.25 | |

a) Asterisks indicate that assignments are not unambiguous. b) In DMSO-$d_6$. c) Acetyl signals: 21.14 and 170.19.

Table 2. $^{13}C$ NMR chemical shifts of the octahydro-1,4-naphthoquinones[a)]

| Compound | **1b** | **2b** | **3b** | **4b** | **5b** | **6b**[b)] | **1c** | **2c** | **3c** |
|---|---|---|---|---|---|---|---|---|---|
| C-1 | 210.37 | 210.77* | 208.91* | 209.56* | 208.91* | 155.50 | 209.24 | 208.66 | 208.91 |
| C-2 | 36.36 | 36.44 | 36.92 | 35.83 | 35.10 | 26.82 | 36.76 | 38.26* | 36.84 |
| C-3 | 36.36 | 37.25 | 36.07 | 36.56 | 37.41 | 36.15 | 36.76 | 37.65* | 36.84 |
| C-4 | 210.37 | 209.80* | 210.61* | 207.85* | 209.80* | 211.26 | 209.24 | 208.66 | 208.91 |
| C-4a | 48.04 | 51.17** | 50.03 | 49.22 | 47.68 | 46.26 | 49.75 | 56.00 | 49.71* |
| C-5 | 25.85 | 33.19 | 36.23 | 41.23 | 41.35 | 40.50* | 26.45 | 31.32 | 34.77 |
| C-6 | 23.45 | 29.42 | 32.18 | 23.98** | 20.08 | 17.53 | 24.75 | 34.00 | 31.36 |
| C-7 | 23.45 | 23.49 | 30.35 | 23.49** | 30.47 | 30.92 | 24.75 | 24.22 | 33.39 |
| C-8 | 25.85 | 26.01 | 23.74 | 26.62 | 31.45 | 26.82 | 26.45 | 26.66 | 26.37 |
| C-8a | 48.04 | 50.52** | 46.01 | 48.41 | 51.13 | 40.86* | 49.75 | 51.25 | 49.46* |
| C-Me | | 18.54 | 22.23 | | 15.82 | 15.25 | | 21.02 | 22.23 |
| COO | | | | 173.60 | 173.52 | 173.36 | | | |
| O-Me | | | | 51.82 | 51.78 | 51.05 | | | |

a) Asterisks indicate that assignments are not unambiguous. b) In DMSO-$d_6$.

Table 3. $^{13}C$ NMR chemical shifts of **7**—**13** and **14b**[a)]

| Compound | **7** | **8** | **9**[b)] | **10**[c)] | **11** | **12** | **13** | **14b**[d)] |
|---|---|---|---|---|---|---|---|---|
| C-1 | 70.45 | 70.20 | 72.31 | 72.07 | 79.57 | 74.14 | 74.70 | 74.22 |
| C-2 | 29.21 | 31.61 | 25.97 | 28.36 | 30.63* | 30.92* | 30.59* | 30.63* |
| C-3 | 38.51 | 37.90 | 38.30 | 37.82 | 32.99 | 33.43 | 25.68 | 22.40 |
| C-4 | 209.48 | 210.94 | 207.85 | 209.56 | 208.66 | 208.59 | 70.36 | 72.72 |
| C-4a | 49.75 | 47.27 | 49.42 | 47.15 | 52.95 | 54.13 | 44.80 | 42.16 |
| C-5 | 42.56 | 42.69 | 42.36 | 42.48 | 40.50 | 40.25 | 36.40 | 37.25 |
| C-6 | 23.98* | 19.55 | 23.65* | 18.95 | 31.32* | 31.45* | 31.57* | 31.53* |
| C-7 | 24.83* | 34.04 | 24.63* | 34.00 | 19.15 | 27.79 | 28.93 | 28.77 |
| C-8 | 21.18 | 27.67 | 21.91 | 28.04 | 29.05 | 33.84 | 34.85 | 34.98 |
| C-8a | 45.69 | 47.56 | 42.36 | 44.15 | 34.33 | 40.25 | 39.81 | 39.85 |
| C-Me | | 17.12 | | 17.00 | | 19.23 | 19.15 | 19.11 |
| COO | 174.57 | 174.57 | 173.85 | 173.93 | 172.30 | 172.39 | 175.84 | 174.41 |
| O-Me | 51.70 | 51.61 | 51.61 | 51.57 | | | | |

a) Asterisks indicate that assignments are not unambiguous. b) Acetyl signals: 21.14 and 170.19. c) Acetyl signals: 21.06 and 170.28. d) Acetyl signals: 21.18 and 170.19.

downfield shifts of the carbons $\beta$ to the double bond in cyclohexenes.[10] Assignment for C-5 in **3b** is based on the $\beta_e$ parameter (9.03 ppm) of the methyl group[1a] and the chemical shift of C-8 in **2b**, since both carbons seem to be similarly affected by the 1,4-cyclohexanedione ring. The situation of C-6 in **2b** is similar to that of C-7 in **3b**, their signals being observed at 29—30 ppm.

Of the two signals for C-2 and -3 in **5a** and **5b**, the signals at lower fields were assigned to C-3, respectively, since they were slightly shifted upfield upon replacement of the C-1 carbonyl with the hydroxyimino group (to **6a** and **6b**). In the spectra of **7** and **8**, the signals shifted upfield upon acetylation were assigned to C-2 and -8a, and the C-8 signals appearing upfield were compared with those in **4b** and **5b** by the $\gamma$-gauche effects of the hydroxyl groups, respectively.[11]

Assignments for C-4a, -7, -8, and -8a in **11** and **12** are based on the Dalling-Grant parameters.[1] The effects of the equatorial methyl group on C-7 and -8a in **12** are in line with the predicted values (C-7: $\beta_e+\beta_e\alpha_a=8.2$ ppm; C-8a: $\beta_e+\alpha_a\beta_e=5.6$ ppm), although the effect on the $\alpha$-carbon is larger than the predicted value (C-8: $\alpha_e+\alpha_e\beta_a=3.1$ ppm) (Table 4). The relatively large downfield shift of C-4a might come from the $\beta_g\gamma_t$ effect. In the spectrum of **13**, the signals shifted upfield upon acetylation (to **14b**) were assigned to C-3 and -4a, and the C-5 signal appearing upfield was compared with that in **12** by the $\gamma$-gauche effect of the hydroxyl group.

As shown in Fig. 1, the large downfield shift of the $\alpha$-carbon of the hydroxyl group in **7** upon lactonization (to **11**) seems due to the characteristic deshielding effect of the lactone group, since the similar trend was observed between methyl *cis*-3-hydroxycyclohexanecarboxylate and 1,3-cyclohexanecarbolactone.[12]

*Conformational Analysis.* The shielding trends of the methyl substituent (Table 4) are useful for conformational analysis. The $\gamma$-effects on C-4a and -6 found in **8** and **10** suggest the axial orientation of the methyl group. The $\delta$-effects observed for C-2 indicate the *syn*-diaxial Me–$CH_2$(C-2) interaction.[13] In contrast to the large upfield shift of C-1 in **12**, the characteristically small $\gamma$-gauche effects of the methyl group on C-1 in **8** and **10** are in line with the observation that the $\gamma$-gauche effects of the hydroxyl group are reduced whenever it is *syn*-diaxial to a $\delta$-carbon.[14] Thus **8** and **10** are thought to exist in a form bearing

TABLE 4. METHYL SUBSTITUENT EFFECTS[a]

| Compound | C-1 | C-2 | C-4a | C-5 | C-6 | C-7 | C-8 | C-8a |
|---|---|---|---|---|---|---|---|---|
| **5b** | −0.65 | −0.73 | −1.54 | 0.12 | −3.90 | 6.98 | 4.83 | 2.72 |
| **8** | −0.25 | 2.40 | −2.48 | 0.13 | −4.43 | 9.21 | 6.49 | 1.87 |
| **10** | −0.24 | 2.39 | −2.27 | 0.12 | −4.70 | 9.37 | 6.13 | 1.79 |
| **12** | −5.43 | 0.29 | 1.18 | −0.25 | 0.13 | 8.64 | 4.79 | 5.92 |
| **2c** | −0.58 | 1.50 | 6.25 | 4.87 | 9.25 | −0.53 | 0.21 | 1.50 |
| **3c** | −0.33 | 0.08 | −0.04 | 8.32 | 6.61 | 8.64 | −0.08 | −0.29 |

a) Values obtained from $\delta_c^{R=Me}-\delta_c^{R=H}$ for the corresponding carbons in each case.

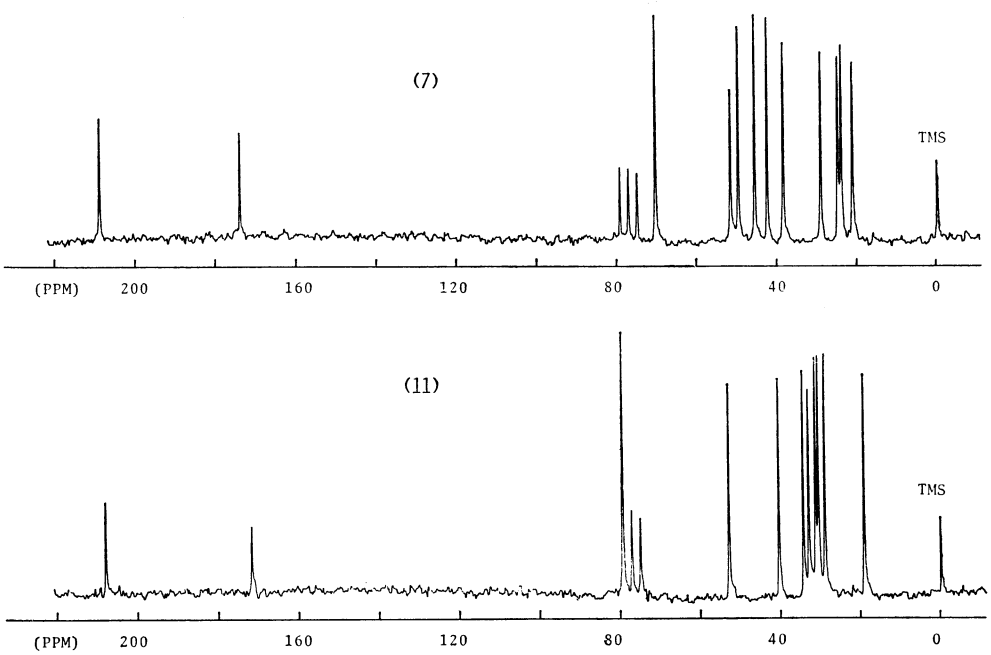
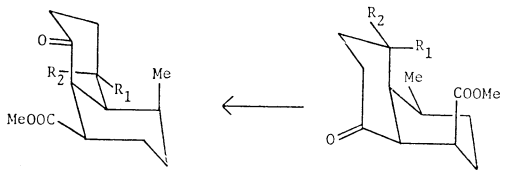



Fig. 1. Proton noise decoupled natural abundance FT $^{13}C$ NMR spectra of **7** and **11** in $CDCl_3$ at 15.04 MHz: pulse width, 25 μs (45°); repetition time 3 s; number of scans, 1000; spectral width, 5000 Hz; data points, 8192; acquisition time, 0.82 .

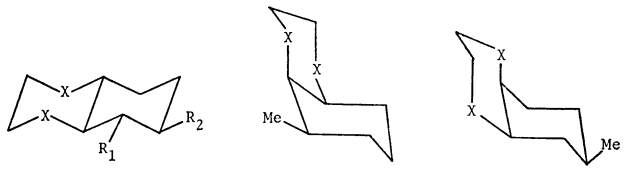


5b $R_1, R_2$=O
8 $R_1$=OH $R_2$=H
10 $R_1$=OAc $R_2$=H

the axial methyl group, as shown above. The estimation is in line with the $^1H$ NMR of **8**.[8]

Conformation of **5b** bearing two substituents in cis relation is of interest, since the conformational distribution of methyl *cis*-4-methylcyclohexanecarboxylate is estimated to be 67% of the equatorial methyl conformer by conformational free energy of a methyl and a methoxycarbonyl group.[12] In **5b**, the $\gamma$-effects of the methyl group are observed on C-4a and -6, the $\beta$-effect on C-8a being smaller than those on C-8a in **12** and C-4a in **2c**. Saturation of the $\Delta^{6,7}$-double bond causes upfield shift of the methyl signal in **5a**, in contrast to the downfield shifts of those in **2a** and **14a**. The chemical shift of C-5 in **5b** is similar to that in **4b** bearing equatorial methoxycarbonyl group. These data indicate that **5b** also exists in a form similar to that of **8** and **10**. Absence of the $\delta$-effect on C-2 might be due to the nonchair conformation of the 1,4-cyclohexanedione ring.[15]

*Comparison with Carbocyclic Analogues.* It is of interest to compare **1c**—**3c**, **2b**, and **3b** with the corresponding decalins (X=$CH_2$).[1b] The chemical shift differences are summarized in Table 5. The $^{13}C$ NMR spectra of decalins were recorded as neat substance, whereas the spectra reported here were obtained in $CDCl_3$. A comparison of the shift values of *trans*-decalin in $CDCl_3$ (26.86, 34.37, and 43.70 ppm) with the literature values of the neat substance (27.17, 34.74, and 44.22 ppm) indicates that the solvent effect is not large.



1c X=CO $R_1, R_2$=H
2c X=CO $R_1$=Me $R_2$=H
3c X=CO $R_1$=H $R_2$=Me

2b X=CO

3b X=CO

The strong shieldings for C-5 and -8 in **1c**—**3c**, and for C-8 in **3b** are similar to that for the methyl group (−9.4 ppm) in 2-methylcyclohexanone,[16] and mainly ascribed to the $\beta$-effect of the carbonyl group. Although the effects of the axial carbonyl group on cyclohexane ring are not clear, the fact that C-7 in **2b** and C-6 in **3b** are shielded indicates the presence of the $\gamma$-effect of the carbonyl group similar to that of oxygen and nitrogen on *anti*-periplanar $\gamma$-carbons.[17] The upfield shifts of C-5 and -7 in **5b** compared with those in **8** might be rationalized by the shielding effect of the C-1 carbonyl group. Accordingly, the upfield shifts of C-6 and -7 in **1c**—**3c** seem to be mainly due to the effect of the carbonyl group at the $\gamma$-position.

On the other hand, C-6 and -8 in **2b**, and C-5 and -7 in **3b** are little affected. The feature might be explained by two opposing effects: shielding by the two carbonyl groups and deshielding due to the absence of the $\gamma_{HH}$ interaction,[1b] the latter being in line with the small chemical shift differences between C-2 and -3 in **2b**—**5b**.

## Experimental

Melting points are uncorrected . The IR spectra were recorded on a Hitachi Infrared Spectrometer EPI-$G_3$ in Nujol. The $^{13}C$ NMR spectra were obtained on a JEOL JNM-PFT-60 (15.04 MHz) at 27 °C. Samples were observed in 10 mm spinning tubes at *ca.* 20% solution in $CDCl_3$, unless otherwise stated. The solvent provided the internal lock signal. The measurement conditions are shown in Fig. 1. All the chemical shifts are expressed in terms of $\delta$(ppm downfield from internal TMS). Each observed chemical shift is estimated to be accurate to $\delta \pm 0.08$.

*Preparation of* ***2a***. A crude adduct[5] formed by 1.00 g of *trans*-1,3-pentadiene and 0.80 g of *p*-benzoquinone was reduced with 5 g of zinc in 20 ml of AcOH at room temperature for 1 h. Work-up in the usual way afforded 1.16 g of **2a**: mp 84—85 °C (from diisopropyl ether); IR 1708 $cm^{-1}$. Found: C,74.08; H, 7.99%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H,7.92%.

*Compound* ***3a***. In a similar way to the preparation of **2a**, a crude adduct[6] formed by 6.81 g of isoprene and 7.00 g of *p*-benzoquinone was reduced with zinc to afford 6.52 g of **3a**: mp 86—87 °C (from hexane); IR 1714 $cm^{-1}$. Found: C, 74.09; H, 8.04%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

*Compound* ***4a***. In a similar way to the preparation of **2a**, 2.00 g of the adduct[7] of methyl 2,4-pentadienoate and *p*-benzoquinone was reduced with zinc to afford 0.92 g of **4a**: mp 130—131 °C (from benzene-hexane); IR 1733 and 1709 $cm^{-1}$. Found: C, 64.64; H, 6.32%. Calcd for $C_{12}H_{14}O_2$: C, 64.85; H, 6.35%.

Table 5. Shift differences[a] between octahydro-1,4-naphthoquinones (X=CO) and decalins (X=$CH_2$)

| Compound | C-4a | C-5 | C-6 | C-7 | C-8 | C-8a | Me |
|---|---|---|---|---|---|---|---|
| **1c** | 5.53 | −8.29 | −2.42 | −2.42 | −8.29 | 5.53 | |
| **2c** | 5.40 | −7.10 | −3.12 | −3.23 | −8.73 | 7.20 | 1.28 |
| **3c** | 6.22 | −8.54 | −1.70 | −2.27 | −7.93 | 6.07 | −0.62 |
| **2b** | 8.19 | −3.99 | −0.12 | −3.93 | 0.24 | 11.82 | −1.24 |
| **3b** | 13.05 | 0.60 | −2.04 | 0.02 | −9.48 | 9.54 | −0.93 |

a) Values obtained from $\delta_c^{X=CO} - \delta_c^{X=CH_2}$ for the corresponding carbons in each case.

*Compound* ***2b***. Hydrogenation of 1.10 g of **2a** with 117 mg of 5% Pd-C in 100 ml of AcOEt afforded 0.84 g of **2b**: mp 55—56 °C (from diisopropyl ether); IR 1718 and 1704 $cm^{-1}$. Found: C, 73.25; H, 9.07%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

*Compound* ***2c***. Treatment of 149 mg of **2b** with 2 ml of 6% methanolic hydrogen chloride at room temperature overnight afforded 48 mg of **2c**: mp 62—63 °C (from petroleum ether); IR 1705 $cm^{-1}$. Found: C, 73.12; H, 9.05%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

*Compounds* ***3b*** *and* ***3c***. Hydrogenation of 1.14 g of **3a** with 165 mg of 5% Pd-C in 80 ml of AcOEt afforded 0.78 g of **3b**: mp 66—67 °C (from diisopropyl ether); IR 1705 $cm^{-1}$. Found: C, 73.44; H, 9.08%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%. The mother liquor was chromatographed on 5 g of $Al_2O_3$. Elution with benzene afforded 0.20 g of **3c**: mp 119—120 °C (from hexane); IR 1707 $cm^{-1}$. Found: C, 73.27; H, 9.16%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

*Preparation of* ***6a***. A mixture of 17.56 g of **5a**,[8] 5.54 g of $NH_2OH \cdot HCl$, and 6.67 g of NaOAc in MeOH–$H_2O$ (400 ml–100ml) was refluxed for 2 h. Concentration of the solution afforded 16.41 g of **6a**: mp 208—209 °C (from MeOH); IR 3480, 1731, and 1708 $cm^{-1}$. Found: C, 61.97; H, 6.84; N, 5.51%. Calcd for $C_{13}H_{17}O_4N$: C, 62.14; H, 6.82; N, 5.57%.

*Compound* ***6b***. Hydrogenation of 2.54 g of **6a** with 65 mg of $PtO_2$ in 300 ml of MeOH afforded 1.55 g of **6b**: mp 211—213 °C (from MeOH); IR 3490, 1736, and 1701 $cm^{-1}$. Found: C, 61.66; H, 7.65; N, 5.49%. Calcd for $C_{13}H_{19}O_4N$: C, 61.64; H, 7.56; N, 5.53%.

*Compound* ***15***. Hydrogenation of 2.89 g of **6a** with 195 mg of $PtO_2$ in 150 ml of AcOH afforded 1.46 g of **15**: mp 199—200 °C (from AcOEt); IR 3430, 3190, and 1668 $cm^{-1}$; $^{13}C$ NMR 19.47(Me), 26.17(C-3), 28.52(C-7), 30.80(C-2*), 32.09(C-6*), 35.26(C-8), 36.88(C-5), 40.17(C-8a), 45.16 (C-4a), 46.91(C-1), 71.54(C-4), and 176.69 ppm (C=O). Found: C, 68.84; H, 9.31; N, 6.95%. Calcd for $C_{12}H_{19}O_2N$: C, 68.86; H, 9.15; N, 6.69%.

*The Acetate* ***10***. Treatment of 310 mg of **8**[8] with 3 ml of $Ac_2O$ and 4 ml of pyridine at room temperature overnight afforded 339 mg of **10**: mp 115—117 °C(from AcOEt–hexane); IR 1737, 1710, and 1249 $cm^{-1}$. Found: C, 63.72; H, 8.00%. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85%.

*The Acetate* ***14b***. In a similar way to the preparation of **10**, 216 mg of **13**[8] was acetylated to afford 229 mg of **14b**: mp 97.5—99 °C (from benzene-hexane); IR 1740, 1717, and 1241 $cm^{-1}$. Found: C, 66.59; H, 8.07%. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99%.

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