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# The Reaction of Methyl *cis*-Decahydro-5,8-dioxonaphthalene-1-carboxylates

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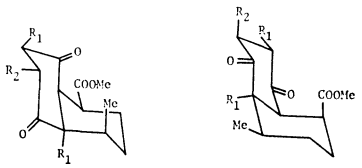
**Synopsis.** Methyl *cis*-decahydro-5,8-dioxonaphthalene-1-carboxylates (**1b** and **1c**) were derived from the Diels-Alder adducts of *p*-toluquinone or *p*-xyloquinone and methyl sorbate, respectively. The $^{13}C$ NMR spectra of **1b** and **1c** suggest the existence of **1b** and **1c** in the form (A), which is in line with the formation of the keto $\gamma$-lactone from **1b** and of the keto alcohol from **1c**.

In our previous paper, the compound **1a**, derived from the Diels-Alder adduct of *p*-benzoquinone and methyl sorbate, was indicated to exist in the form (A) shown below.[1a] This paper deals with the conformation and reaction of methyl *cis*-decahydro-5,8-dioxonaphthalene-1-carboxylates (**1b** and **1c**).

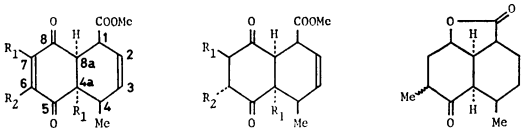


(A) (B)

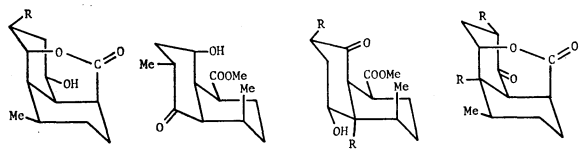
**1a** $R_1,R_2=H$
**1b** $R_1=H$, $R_2=Me$
**1c** $R_1=Me$, $R_2=H$

The adduct (**2a**) of *p*-toluquinone and methyl sorbate was reduced with zinc to **3a**, which was converted into **1b** by catalytic hydrogenation with palladium-carbon. The Diels-Alder reaction of *p*-xyloquinone and methyl sorbate was catalyzed by aluminium chloride to afford **2b**, which was similarly reduced to **3b** and **1c**. The cis ring junction of **2b** is supported by the comparison of the physical data with those of the C-8a epimer of **2b**.[2]

The treatment of **1b** with sodium borohydride at room temperature for 2 h gave the keto $\gamma$-lactone (**4**), and that for 3 days afforded the $\delta$-lactone (**5a**), which was also obtained from **4** by further treatment with sodium borohydride. The formation of **4** suggests that the methyl group originally in *p*-toluquinone is situated at C-6 in the adduct **2a**, since the C-8 carbonyl group was reduced more easily than the C-5 carbonyl group in **1b**. The $^{13}C$ NMR chemical shifts of **5a** are similar to those of **5b**[1a] within 1 ppm except for C-5, -6, and -7, which are shifted downfield by the $\alpha$- and $\beta$-effects of the methyl group at C-6 in **5a**. Absence of the $\gamma$-effect on C-4a and -8 by the methyl group at C-6 in **5a** indicates the equatorial orientation of the methyl group.[3] The



**2a** $R_1=H$, $R_2=Me$ **3a** $R_1=H$, $R_2=Me$ **4**
**2b** $R_1=Me$, $R_2=H$ **3b** $R_1=Me$, $R_2=H$



**5a** R=Me **6** **7a** R=Me **8a** R=Me
**5b** R=H **7b** R=H **8b** R=H

$^{13}C$ chemical shift differences within 1 ppm for C-1, -3, -4, -4a, and -8a between **1a**[1a] and **1b** indicate that **1b** also exists in the form (A) with the stable equatorial methyl group at C-6. Accordingly, **4** is formed from the reduction intermediate (**6**) which is unstable because of the steric interaction between the hydroxyl group at C-8 and the methyl group at C-4. Formation of **5a** proceeds through the ring inversion, epimerization at C-6, and reduction of the C-5 carbonyl group in **6**.

On the other hand, sodium borohydride reduction of **1c** afforded the keto alcohol (**7a**), which was converted into the $\delta$-lactone (**8a**) by methanolic hydrogen chloride. The formation of **8a** from **1c** *via* **7a** is similar to that of **8b** from **1a** *via* **7b**.[1b] It is supported by the $^{13}C$ NMR spectra of **7a** and **1c** that two methyl groups originally in *p*-xyloquinone are situated at C-4a and -7 in the adduct **2b**, since the signals for C-4a and -6 in **7a** are shifted upfield compared with those in **1c**. Comparison of the $^{13}C$ chemical shifts of **1c** with **1b** suggests that **1c** also exists in the form (A), since the signal for C-3 in **1c** is shifted upfield by the $\gamma$-gauche effect of the methyl group at C-4a. The axial proton signal at 4.02 ppm (–CH–OH, q, $J=11$ and 6 Hz) in the $^1H$ NMR spectrum of **7a** is in line with the $^{13}C$ signal for C-4 in **7a**

TABLE 1. $^{13}C$ CHEMICAL SHIFTS OF **1b**, **1c**, AND **7a**

| Compound | **1b** | **1c** | **7a** |
|---|---|---|---|
| C-1 | 40.82* | 38.39* | 38.59* |
| 2 | 17.89 | 18.38 | 19.19 |
| 3 | 31.45 | 27.43 | 30.72 |
| 4 | 30.76 | 34.65 | 32.54 |
| 4a | 50.97 | 51.90 | 46.46 |
| 5 | 211.91** | 213.12** | 77.06 |
| 6 | 41.06* | 44.43 | 41.31 |
| 7 | 42.24 | 39.76* | 41.31* |
| 8 | 208.83** | 211.18** | 211.59 |
| 8a | 47.44 | 52.55 | 52.91 |
| COO | 173.69 | 174.25 | 175.31 |
| OMe | 51.78 | 51.78 | 51.70 |
| $C_4$–Me | 15.05 | 16.80 | 18.50 |
| $C_{4a}$–Me | | 26.01 | 28.81 |
| $C_6$–Me | 13.31 | | |
| $C_7$–Me | | 16.80 | 14.36 |

*, ** Assignments are not unambiguous within indicated pair(s).

which is shifted upfield (−2.11 ppm) compared with that in **1c** by the $\gamma$-gauche effect of the hydroxyl group. Accordingly, lactonization of **7a**, which is stable in contrast to **6**, proceeds by the aid of acid through the ring inversion and epimerization at C-7.

Therefore, the formation of **4** and **7a** is in line with the structures of **1b** and **1c** in the form (A).

## Experimental

Melting points are uncorrected. The IR spectra were recorded on a Hitachi infrared spectrometer EPI-$G_3$ in Nujol, unless otherwise stated. The $^1H$ and $^{13}C$ NMR spectra were obtained on a JEOL JNM-PFT-60 in $CDCl_3$. All the chemical shifts are expressed in term of $\delta$ (ppm downfield from internal TMS).

*Preparation of* ***2a.*** A solution of 12.2 g of *p*-toluquinone and 12.6 g of methyl sorbate in 150 ml of benzene was refluxed for 30 h, and concentrated *in vacuo* to afford 7.80 g of **2a**: mp 108—110 °C (from EtOH); IR 1730 and 1678 $cm^{-1}$; $^1H$ NMR 0.78 (3H, d, $J$=7 Hz), 2.01 (3H, d, $J$=1.5 Hz), 3.74 (3H, s), 5.70 (1H, m), 6.20 (1H, br d, $J$=11 Hz), and 6.67 ppm (1H, d, $J$=1.5 Hz). Found: C, 67.59; H, 6.48%. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%.

*Preparation of* ***3a.*** Treatment of 2.00 g of **2a** with 10 g of zinc in 50 ml of AcOH at room temperature for 3 h afforded 1.86 g of **3a**: mp 148—150 °C (EtOH); IR 1734 and 1708 $cm^{-1}$; $^1H$ NMR 0.74 (3H, d, $J$=7 Hz), 1.16 (3H, d, $J$=6 Hz), 3.73 (3H, s), 5.70 (1H, m), and 6.10 ppm (1H, br d, $J$=10 Hz). Found: C, 67.09; H, 7.35%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

*Preparation of* ***1b.*** Hydrogenation of 1.22 g of **3a** with 150 mg of 5% Pd-C in 70 ml of MeOH afforded 1.04 g of **1b**: mp 169—170 °C (in a sealed tube) (EtOH); IR 1732 and 1707 $cm^{-1}$; $^1H$ NMR 0.67 (3H, d, $J$=7 Hz), 1.13 (3H, d, $J$=6 Hz), and 3.70 ppm (3H, s). Found: C, 66.71; H, 8.07 %. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99%.

*Preparation of* ***2b.*** To an ice-cold suspension of 1.3 g of powdered anhydrous $AlCl_3$ in 50 ml of dry benzene was added 4.04 g of *p*-xyloquinone and then 3.61 g of methyl sorbate. The mixture was stirred at room temperature for 3 days. Work-up in the usual manner[4] afforded 1.48 g of **2b**: mp 134—136 °C (EtOH); IR 1738 and 1673 $cm^{-1}$; $^1H$ NMR 0.75 (3H, d, $J$=7 Hz), 1.41 (3H, s), 1.99 (3H, d, $J$=1.5 Hz), 3.75 (3H, s), 5.60 (1H, m), 6.20 (1H, dd, $J$=10 and 1 Hz), and 6.57 ppm (1H, d, $J$=1.5 Hz). Found: C, 68.68; H, 6.95 %. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92%.

*Preparation of* ***3b.*** Treatment of 1.11 g of **2b** with 5 g of zinc in 50 ml of AcOH at room temperature for 2 h afforded 0.88 g of **3b**: mp 102—103 °C (EtOH); IR 1733 and 1075 $cm^{-1}$; $^1H$ NMR 0.77 (3H, d, $J$=7 Hz), 1.15 (3H, d, $J$=6 Hz), 1.36 (3H, s), 3.73 (3H, s), 5.60 (1H, m), and 6.16 ppm (1H, br d, $J$=10 Hz). Found: C, 67.89; H, 7.64%. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%.

*Preparation of* ***1c.*** Hydrogenation of 783 mg of **3b** with 81 mg of 5% Pd-C in 40 ml of MeOH afforded 681 mg of **1c**: mp 78—79 °C diisopropyl ether); IR 1730 and 1708 $cm^{-1}$; $^1H$ NMR 0.73 (3H, d, $J$=7 Hz), 1.16 (3H, d, $J$=7 Hz), 1.40 (3H, s), and 3.68 ppm (3H, s). Found: C, 67.41; H, 8.40%. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33%.

*$NaBH_4$ Reduction of* ***1b*** *to* ***4.*** Treatment of 620 mg of **1b** with 170 mg of $NaBH_4$ in 50 ml of MeOH at room temperature for 2 h afforded 457 mg of **4**: mp 187—188 °C (benzene); IR 1764 and 1701 $cm^{-1}$; $^1H$ NMR 1.19 (6H, d, $J$=6 Hz) and 4.70 ppm (1H, m, $W_H$=10 Hz). Found: C, 70.05; H, 8.31 %. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

*$NaBH_4$ Reduction of* ***1b*** *to* ***5a.*** Treatment of 507 mg of **1b** with 520 mg of $NaBH_4$ in 50 mg NeOH at room temperature for 3 days afforded 211 mg of **5a**: mp 169—170 °C (benzene); IR($CHCl_3$) 3430 and 1723 $cm^{-1}$; $^1H$ NMR 1.07 (6H, d, $J$=5 Hz), 2.97 (1H, br s, $W_H$=8 Hz), 3.21 (1H, br s, OH), 3.80 (1H, m, $W_H$=18 Hz), and 4.42 ppm (1H, br s, $W_H$=4 Hz); $^{13}C$ NMR 17.81 ($C_6$-Me), 19.23 ($C_4$-Me), 29.09 (C-3), 31.57 (C-2), 34.25 (C-7), 34.81 (C-4), 36.19 (C-6*), 36.56 (C-1*), 40.21 (C-4a), 44.35 (C-8a), 70.24 (C-8), 79.09 (C-5), and 175.63 ppm (COO). Found: C, 69.60; H, 9.22%. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%. In a similar way, **5a** was obtained from **4** (95 mg from 173 mg of **4**).

*$NaBH_4$ Reduction of* ***1c*** *to* ***7a.*** Treatment of 504 mg of **1c** with 160 mg of $NaBH_4$ in 20 ml of MeOH at room temperature for 4 h afforded 380 mg of **7a**: mp 124—125 °C (diisopropyl ether); IR 3510, 1728, and 1711 $cm^{-1}$; $^1H$ NMR 0.95 (3H, d, $J$=7 Hz), 1.00 (3H, d, $J$=6 Hz), 1.37 (3H, s), 3.65 (3H, s), and 4.02 ppm (1H, q, $J$=11 and 6 Hz). Found: C, 66.93; H, 9.22%. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02%.

*Lactonization of* ***7a*** *to* ***8a.*** Treatment of 339 mg of **7a** with 3 ml of 5% methanolic hydrogen chloride at room temperature overnight afforded 195 mg of **8a**: mp 74—75 °C (diisopropyl ether); IR 1717 and 1709 $cm^{-1}$; $^1H$ NMR 0.90 (3H, s), 1.10 (6H, d, $J$=6 Hz), and 4.68 ppm (1H, d, $J$=2 Hz, $W_H$=6 Hz); $^{13}C$ NMR 13.59 ($C_7$-Me), 15.42 ($C_4$-Me). 24.06 ($C_{4a}$-Me), 29.62 (C-3), 31.08 (C-2), 36.60 (C-7*), 37.17 (C-6), 38.63 (C-4a), 41.55 (C-1 and -4*), 59.53 (C-8a), 78.84 (C-5), 172.87 (COO), and 211.26 ppm (C-8). Found: C, 71.12; H, 8.77%. Calcd for $C_{14}H_{20}O_3$; C, 71.16; H, 8.53%.

## References

1) a) H. Irikawa and Y. Okumura, *Bull. Chem. Soc. Jpn.*, **51**, 2086 (1978); b) H. Irikawa and Y. Okumura, *ibid.*, **51**, 657 (1978).

2) F. Bohlmann, W. Mathar, and H. Schwarz, *Chem. Ber.*, **110**, 2028 (1977).

3) D. K. Dalling, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **95**, 3718 (1973).

4) I. Nagakura, H. Ogata, M. Ueno, and Y. Kitahara, *Bull. Chem. Soc. Jpn.*, **48**, 2995 (1975).