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PREFERRED CONFORMATIONS OF 9-OXO-8,9,10,11-TETRAHYDRO- AND 9-HYDROXY-10,11-DIHYDRO-7H-CYCLOOCTA[de]NAPHTHALENE-8,10-DICARBOXYLIC ESTERS: UNUSUALLY STABLE TAUTOMERS OF β-KETOESTERS

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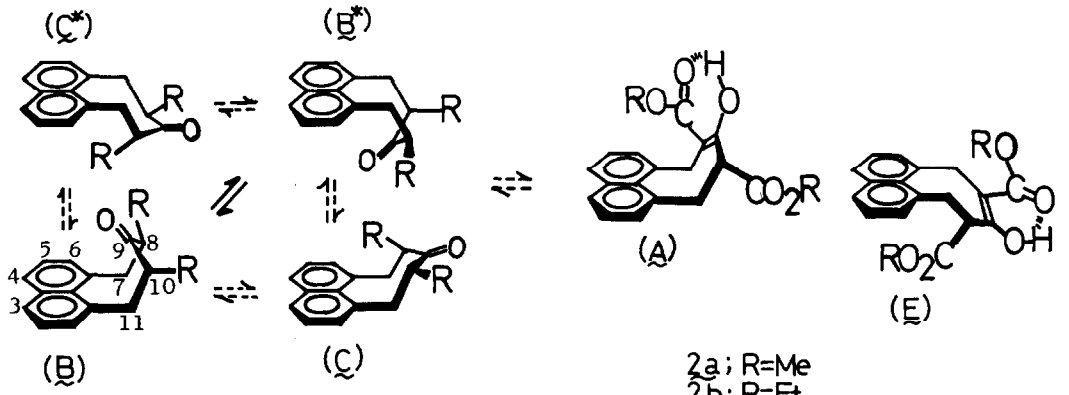
It is well known that β-ketoesters assume both ketonic and enolic structures by tautomerization and such keto-enol equilibria have hitherto been observed in a number of cyclic and acyclic enolizable β-ketoesters.[1] However, most compounds reported so far exist only as an equilibrium mixture of the keto and enol form,[1] or assume only either form of the two isomers.[2,3] As yet, such a case is not known that the two isomers are so stable that they are obtained separately even in solution. During our studies of pericyclic naphthalene chemistry,[4-6] it was found that the titled tautomers are unusually stable compared to those reported before. In this paper, we report the preferred conformations of these tautomers based on the NMR spectra.

1,8-Bis(bromomethyl)naphthalene was reacted with acetonedicarboxylic esters in the presence of sodium ethoxide to give keto form (1), which then is coverted to the corresponding enol form (2) quantitatively by treating with sodium ethoxide followed by hydrochloric acid. Compounds (1a-2b) were characterized by physical and IR data shown in Table 1.[7] As can be seen in the table, the IR spectra of 1 in chloroform solution show absorptions characteristic of the ketonic tautomers alone, while the absorptions in the spectra of 2 are attributable solely to the chelated enols. It is thus suggested that each tautomer of 1a-2b is, even in solution, stable enough not to undergo a ready isomerization at ambient temperature. This result is also shown by NMR spectra, by which the conformations of each tautomer can be obtained.

^{1}H-NMR spectrum of 1a at ambient temperature shows a singlet for the methyl group and a broad signal for peri ring protons. As the temperature is lowered, the methyl signal broadens and then splits into a doublet of equal intensities, while ring protons show complex signals characteristic of two types C$\underline{H}_2$ and C$\underline{H}$ groups (Table 2). On the other hand, the proton decoupled ^{13}C-NMR spectrum of 1a at 30° in the high field region consists of 3 lines due to the $\underline{C}H_3$, $\underline{C}H_2$ and $\underline{C}H$ carbons respectively, all of which split into 1:1 doublets below -40°.

These spectra suggest that 1a exists in a trans (unsymmetrical) form inverting rapidly at room temperature. An interior H-11 proton of 1a, which is deshield-



ed greatly as a result of steric compression,[4-6] is coupled strongly (12.6 Hz) with an adjacent H-10 methine proton. Thus the ground-state conformation of 1a is boat (B), where the H-10 proton is equatorial with trans relationship to the interior H-11 proton.[4-6] A small J-value (8.1 Hz) between an interior H-7 and a H-8 methine proton suggests that the H-8 proton is axial. Similar result was obtained for 1b (Table 2).

Conformation (B) is consistent with ^{13}C chemical shift values shown in Table 2. Thus a high-field shift of C-7 signal relative to that of C-11 is due to a gauche interaction between an equatorial COOR on C-8 and the peri bond.[6] The C-8, which is shielded by this interaction, suffers an additional shielding arising from an eclipsed interaction between the C=O and the equatorial COOR.[6] Besides, it is further shielded by a γ-gauche effect associated with an axial COOR on C-10.[6] As a result, the C-8 signal appears at a much higher field than C-10.

The unusually greater stability of (B) over (C) observed in 1 results chiefly from much lower torsional energy about C_7-C_8 and C_{10}-C_{11} bonds of the boat conformation than the chair, which is one of the characteristic features in the peri-8 ring system as described before.[4-6] In addition, the closeness of the axial COOR to the naphthalene ring in (C) makes this conformation much less stable than (B). None of the cis isomers was obtained for 1, probably because dipolar interactions of carbonyl groups are more serious in these conformations than in the trans isomers. The boat inversion (B⇌B*) in 1 may proceed by pseudorotations of the peri bonds via the twist-boat as in the parent ketone (3)[5] and in related compounds.[6]

On the other hand, the spectra of the enols (2) are invariant of temperature, indicating that 2, in contrast to 1, undergoes none of the appreciable ring inversions at ambient temperature. A strong coupling between an interior H-11 and an adjacent H-10 proton suggests that 2 exists only in pseudoaxial conformation (A) where a dihedral angle between these protons is ~150°. Another conformation (E),

Table 1. IR Data of 1a-2b in $CHCl_3$ and Nujol.[a]

	mp(°C)	ester νC=O	ketone νC=O	chelated conjugated νC=O	conjugated νC=C
1a[b]	136.5-138	1745 (1741)	1721 (1710)		
1b[b]	146-147	1741 (1742)	1719 (1707)		
2a[c,e]	125-126.5	1736 (1743)		1658 (1649)	1621 (1619)
2b[c,e]	113-115	1734 (1737)		1654 (1646)	1619 (1619)
3[d]	195-196		1703 (1695)		

[a]Values in parenthesis. [b]Colorless fine needles. [c]Slightly colored prisms. [d]Ref. 5. [e]OH stretching absorptions are strongly perturbed beyond recognition.

Table 2. ^{1}H- and ^{13}C-NMR Data of 1a-2b in $CDCl_3$.[a]

	H-7-in	H-7-ex	H-8	H-10	H-11-in	H-11-ex	CH_3	OH
1a[b]	4.39dd J=15.3 8.1	3.64d J=15.3	4.70d J=8.1	3.62dd J=12.6 4.0	4.73dd J=14.4 12.6	3.41dd J=14.4 4.0	3.85s 3.76s	
1b[b]	4.38dd J=15.3 8.0	3.62dd J=15.3 1.0	4.60d J= 8.0	3.60dd J= 12.3 5.0	4.68dd J=14.9 12.3	3.42dd J=14.9 5.0	1.26t 1.33t	
2a[c]	4.80d J=16.0	3.78d J=16.0	....	3.87dd J=12.7 6.1	4.31dd J=14.0 12.7	3.25dd J=14.0 6.1	3.83s 3.67s	12.57s
2b[c]	4.80d J=15.9	3.78d J=15.9	....	3.86dd J=12.9 6.2	4.30dd J=14.0 12.9	3.26dd J=14.0 6.2	1.34t 1.27t	12.63s

	C-7	C-8	C-9	C-10	C-11	-COO-	-OCH_2-	CH_3
1a[d]	34.9	52.6	202.5	62.0	37.0	171.2 169.4		53.6 53.5
1b[d]	35.2	53.7	202.5	61.6	36.9	170.9 168.8	62.3	14.0
2a[c]	31.7	103.5	169.4	54.6	38.0	173.6 171.6		52.8 51.8
2b[c]	31.6	103.4	169.3	54.7	37.8	173.0 171.0	60.8 61.7	14.0 14.1
3[e]	34.1	46.0	213.9	46.0	34.1			

[a]δ from internal TMS, J in Hz. [b]At -50.3°. [c]At 30.0°. [d]At -61.5°. [e]Ref. 5.

which is also possible for 2 by ring inversion, seems less favored because of a greater proximity of the C-10 COOR to the naphthalene nucleus.

It is noted that 1 shows unusually high IR frequencies in both the ketone and ester carbonyl vibrations as compared to 3 and 2 respectively (Table 1). This clearly means that (B) also involves a severe dipolar interaction within molecules, most of which perhaps is derived from the equatorial COOR and the ketone.[1] Marked shieldings of the ketone carbon in 1 relative to that of 3[5] and its 8-alkyl-derivatives[6] should be accounted for chiefly by this interaction.

On the contrary, molecules of 2 may be greatly stabilized by the H-bonded chelated structure as evidenced by a strongly perturbed OH absorption[1] and a greatly deshielded OH signal together with other features shown in the table. This accounts for a large difference in conformational mobility between 1 and 2 observed in the spectra. This is in sharp contrast to other previously reported β-ketoesters with a conformationally rigid polycyclic ring system, which exist both in crystalline state and in solution in a completely enolized form owing to the dipolar interaction of carbonyl groups.[2]

Moreover, conformations of (B) and (A) adequately explain the base catalyzed coversion of 1 to 2; the enolization occurs preferentially at C-8 position having an axial hydrogen of the keto form[8] to give the enol, resulting in a relief of repulsive strains due to the carbonyl groups of the ketone and equatorial COOR.

IR studies revealed that a chloroform solution of 1 contained a small amount of 2 on standing overnight at room temperature, while 2 was slightly changed into 1 under the same experimental condition. Detailed studies on kinetics of the keto-enol transformation and the ring inversion will be reported in a full paper.

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