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Structure Elucidation of Acetylation Products of 2-Acyl-1,3-indanediones by Correlation of Infrared Spectral Data

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Summary. 2-(1-Acetoxyalkylidene)- and 2-(1-acetoxybenzylidene)-1,3-indanediones (**1 a**–**1 e**) were proven to be the products of acetylation of 2-acyl-1,3-indanediones (**2 a**–**2 e**) by ketene using a detailed investigation and correlation analysis of infrared spectral data as well as ^{1}H-NMR and ^{13}C-NMR spectra. Study by means of CNDO/2 and MMPI methods also demonstrates that the structure **1** is more stable as the alternative one of 2-acyl-3-acetoxy-2-indene-1-ones (**5**). It was shown that the recently proposed general correlations $\nu(C=O)_s$ vs. $\nu(C=O)_{as}$ and $\bar{\nu}(C=O)$ vs. $\Sigma X^+(R)$ as well as the mechanical anharmonicities of asymmetric C = O stretching vibration can be successfully used as a tool of structural diagnostics of cyclic 1,3-dicarbonyl compounds.

Keywords. 2-(1-Acetoxyalkylidene)- and 2-(1-acetoxybenzylidene)-1,3-indanediones; Infrared correlation; NMR spectra; CNDO/2; MMPI.

Strukturaufklärung von Acetylierungsprodukten von 2-Acyl-1,3-indandionen mittels Korrelation von Infrarot-Daten

Zusammenfassung. 2-(1-Acetoxyalkyliden)- und 2-(1-Acetoxybenzyliden)-1,3-indandione (**1 a**–**1 e**) wurden mittels einer detaillierten infrarot-spektroskopischen Untersuchung (IR-Korrelation) und ^{1}H-NMR und ^{13}C-NMR Spektroskopie als Acetylierungsprodukte von 2-Acyl-1,3-indandionen (**2 a**–**2 e**) mit Keten nachgewiesen. CNDO/2- und MMPI-Rechnungen zeigten auch, daß Struktur **1** stabiler ist, als die der alternativen 2-Acyl-3-acetoxy-2-inden-1-one **5**. Es wird gezeigt, daß die kürzlich vorgeschlagenen allgemeinen Korrelationen $\nu(C=O)_s$ gegen $\nu(C=O)_{as}$ und $\bar{\nu}(C=O)$ gegen $\Sigma X^+(R)$ und auch die mechanischen Anharmonizitäten der asymmetrischen C = O Streckschwingung erfolgreich als Werkzeug zur Strukturaufklärung cyclischer 1,3-Dicarbonyl-Verbindungen eingesetzt werden können.

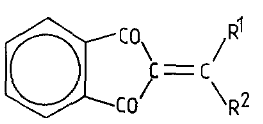
Introduction

Recently [1] the correlation between the symmetric and asymmetric C = O stretching frequencies has been successfully used to distinguish the structure of 3-(N,N-dimethylamino)coumarine from that of the hypothetic 2-(N,N-dimethylamino)-1,3-indanedione. It was also found [2–4] that the mechanical anharmonicity of carbonyl stretching vibrations can be used as an evidence of a vibrationally coupled 1,3-dicarbonyl system.

These methods are applied to determine the structure of ketene acetylation products of 2-acyl-1,3-indanediones **2 a**–**2 e** [5]. For this purpose the fundamental carbonyl stretching frequencies $\nu_{01}(C=O)$ and their first overtones $\nu_{02}(C=O)$ were measured in tetrachloro- and trichloromethane solutions for compounds **1**–**3** and compared with data taken from literature [6, 7]. The representative compounds of alternative structures were investigated using CNDO/2 [8] and MMPI calculations [9] with standard parameterization.

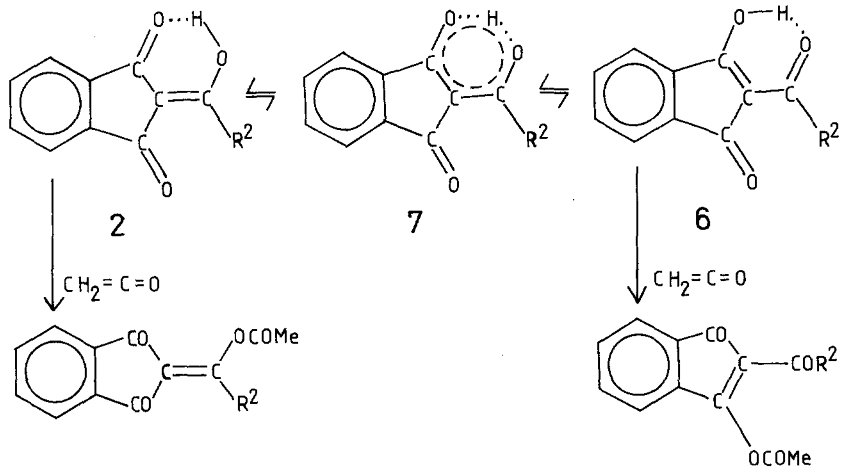
Experimental

The preparation of compounds **1a**–**1e** was described [5]. The 2-acyl-1,3-indanediones **2a**–**2e** were synthesized according to [10]. Compound **3** was prepared by dissolving **2a** (8.7 mmol) in hot ethanol (20 cm^3). By cooling to room temperature a pale-yellow crystalline compound precipitated and after filtering off it was dried under reduced pressure. Yield = 1.4 g (74%), m.p. 163–166.5°C. For $C_{13}H_{12}O_3$ (M=216.2) calculated: C 72.20, H 5.59; found C 72.50, H 5.49. ^{1}H-NMR, δ/ppm: 7.97–7.52 (4 H, m, arom.), 4.40 (2 H, q, J=7 Hz, $-CH_2O-$), 2.77 (3 H, s, CH_3COO-), 1.52 (3 H, t, J=7 Hz, CH_3-). All substances were purified by crystallization prior to the spectral measurements.



1: R^1=OCOMe
2: R^1=OH
1a, 2a: R^2=Me
1b, 2b: R^2=Et
1c, 2c: R^2=Bu^i
1d, 2d: R^2=Bu^t
1e, 2e: R^2=Ph
3: R^1=OEt, R^2=Me
4: R^1=H, R^2=Ph

The infrared spectra of CCl_4 and $CHCl_3$ solutions in the regions of 1 800–1 600 cm^{-1} and 3 600–3 200 cm^{-1} were measured on a Zeiss M-80 spectrometer using NaCl cells of 0.1, 1.0, 20, and 100 mm thickness. The concentration of the solutions were chosen to give maximal absorption between 70%–75%. P.a. solvents were purified and dried in the usual manner. Peak positions were determined with an accuracy of ±0.1 cm^{-1} in the 1 800–1 600 cm^{-1} region and of ±0.5 cm^{-1} in the 3 600–3 200 cm^{-1} region. The ^{13}C-NMR and ^{1}H-NMR spectra were measured in $CDCl_3$ with a Varian VXR-300 instrument operating at 299.93 MHz for ^{1}H nuclei and 75.43 MHz for ^{13}C nuclei; the internal reference was tetramethylsilane.



1

5

Results and Discussion

By acetylation of 2-acyl-1,3-indanediones with ketene [5] two different products, **1** or **5**, can be formed in principle, which depends on the existence of two possible enol-forms **2** or **6** of the starting 2-acyl-1,3-indanediones. According to Refs. [6, 7, 11, 12] the enol-forms **2** or **6** are stabilized by intramolecular hydrogen bonding, which is connected more or less with a delocalization of π- and n-electrons in the six-membered ring of **7**.

It depends only on the type and the conditions of the reaction which of the two forms **2** or **6** will be preferred and attacked by the reagent. E.g. the electroreduction of the enolat-anion of 2-acetyl-1,3-indanedione takes place [12] preferably with the enol-form **6**. On the other hand, it is supposed [7] that 2-acyl-1,3-indanediones in 1,2-dichloroethane solutions undergo enolization (i.e. a reversible autoprotolytic reaction) towards the form **2**. This suggestion was based on the results of an infrared spectral investigation, as well as on the higher electron density on the oxygen atom of the acetyl group in the keto-form of 2-acyl-1,3-indanediones as calculated by the HMO method.

The fundamental carbonyl stretching frequencies ν_{O1} $(C=O)$ of the acetylation products **1a**–**1e** together with those of the starting 2-acyl-1,3-indanediones **2a**–**e** and related compounds **3** and **4** measured in tetrachloro- and trichloromethane solutions are given in Tables 1 and 2. The 1,3-dicarbonyl system of the compound mentioned above exhibits a doublet in the region of $C=O$ stretching frequencies,

Table 1. Fundamental stretching frequencies of cyclic 1,3-dicarbonyl system in CCl_4 (cm^{-1}) and substituent constants for compounds **1**–**4**

Compound	ν_{O1} $(C=O)_{exp.}$[a]				ΣX^+ (R)	ν_{O1} $(C=O)_{calc.}$[b]					
	ν_{as}	ν_s	$\Delta\nu$[c]	$\bar{\nu}$[d]		ν_{as}	$\Delta\nu_{as}$[e]	ν_s	$\Delta\nu_s$[e]	$\bar{\nu}$[d]	$\Delta\bar{\nu}$[e]
1a	1692.8	1 736.0	43.2	1 714.4	3.149	1 694.2	1.4	1 734.9	1.1	1 714.3	0.1
1b	1 692.8	1 736.0	43.2	1 714.4	3.187	1694.2	1.4	1 734.9	1.1	1 716.1	1.7
1c	1 692.8	1 731.2	38.6	1 712.0	3.197	1688.1	4.7	1 734.9	3.7	1 715.8	3.8
1d	1 692.0	1 731.2	39.2	1 711.6	3.263	1688.5	3.5	1 733.9	2.7	1 718.6	7.0
1e	1 697.6	1 736.0	38.4	1 716.8	3.714	1694.6	3.0	1 738.3	2.3	1 715.3	1.5
2a	1 656.0	1 712.8	56.8	1 684.4	2.986	1 664.5	8.5	1 706.1	6.7	1 709.4	25.0
2b	1 656.0	1 710.4	54.5	1 683.2	2.993	1 661.5	5.5	1 706.1	4.3	1 709.7	26.5
2c	1 656.0	1 710.4	54.5	1 683.2	2.993	1 661.5	5.5	1 706.1	4.3	1 709.7	26.5
2d	1 644.0	1 705.6	61.6	1 674.8	3.001	1 655.3	11.3	1 696.8	8.8	1 711.6	36.8
2e	1 651.2	1 712.8	61.6	1 682.0	3.009	1 664.5	12.3	1 702.4	10.4	1 711.9	29.9
3	1 668.0	1 714.4	46.4	1 691.2	3.016	1 666.6	1.4	1 715.5	1.1	1 710.4	4.0
4	1 694.0[f]	1 735.0[f]	41.0	1 714.5	3.169	1 693.0	1.0	1 735.8	0.8	1 715.5	1.0

[a] Experimental values

[b] Calculated using Eq. (1) and Eq. (2)

[c] Frequency separation $\Delta\nu = \nu_s - \nu_{as}$

[d] Arithmetic mean $\bar{\nu} = (\nu_s + \nu_{as})/2$

[e] Absolute value of the difference between the experimental and calculated data

[f] Taken from [4]

Table 2. Fundamental stretching frequencies of the cyclic 1,3-dicarbonyl system in $CHCl_3$ (cm^{-1}) for compounds **1**, **2**, and **4**

Compound	$\nu_{O1}(C=O)$ exp[a]			$\nu_{O1}(C=O)_{calc.}$[b]			
	ν_{as}	ν_s	$\Delta\nu$[c]	ν_{as}	$\Delta\nu_{as}$[e]	ν_s	$\Delta\nu_s$[e]
1a	1 688.8	1 731.2	42.4	1 688.5	0.3	1 731.4	0.2
1b	1 688.8	1 736.0	47.2	1 694.6	5.8	1 731.4	4.5
1c	1 689.6	1 731.2	41.6	1 688.1	1.5	1 732.4	1.2
1d	1 688.0	1 729.6	41.6	1 686.0	2.0	1 731.1	1.5
1e	1 685.6	1 731.2	45.6	1 688.1	2.5	1 729.2	2.0
2a	1 656.0	1 710.2	54.2	1 661.2	5.2	1 706.1	4.1
2b	1 653.5	1 707.5	54.0	1 657.7	4.2	1 704.2	3.3
2c	1 654.8	1 709.8	55.0	1 660.7	5.9	1 705.2	4.6
2d	1 654.5	1 705.0	50.5	1 654.5	0.0	1 705.0	0.0
2e	1 645.5	1 710.4	64.9	1 661.5	16.0	1 697.9	12.1
4	1 690.0[f]	1 733.0[f]	43.0	1 690.4	0.4	1 732.7	0.3

[a–c, e, f] See Table 1

which can be a priori assigned to the symmetric (in-phase) (ν_s) and asymmetric (out-of-phase) (ν_{as}) vibrations. Besides of these bands for compounds **1** an additional higher-frequency maximum is observed in the region of 1 791.2–1 779.2 cm^{-1} in CCl_4 and 1 777.6–1 770.4 cm^{-1} in $CHCl_3$, which corresponds to the carbonyl stretching vibration of the acetoxy group.

We have earlier found [13, 14] that a general empirical relationship exists [Eq. (1)] between the symmetric and asymmetric carbonyl stretching frequencies of 1,3-indanedione derivatives,

$$\nu_s(C=O) = 0.781\,\nu_{as}(C=O) + 412.8\,. \qquad (1)$$

The validity of Eq. (1) was proven [12] for 406 experimental points obtained for a variety of 1,3-indanedione derivatives by measurements in various solvents.

As the values of $\Delta\nu_s$ and $\Delta\nu_{as}$ indicate, the application of Eq. (1) to the series given in Tables 1 and 2 (measured in both $CHCl_3$ and CCl_4 solutions) leads to an excellent correlation for compounds **1**, **3** and **4** and to a satisfactory accordance for the majority of substances **2**. Similarly the carbonyl stretching frequencies of other 2-acyl-1,3-indanediones [6, 7] behave fairly well according to Eq. (1). From these results it follows that in all investigated compounds the carbonyl groups are settled within a 1,3-indanedione cycle with mechanically coupled C=O stretching vibrations. This means that the structure **1** is preferred over **5**. It is evident however, that the intramolecular hydrogen bonding in 2-acyl-1,3-indanediones does not violate substantially the validity of the $\nu_s(C=O)$ vs. $\nu_{as}(C=O)$ correlation, which can be described better by structure **2**.

It is also known [15] that the arithmetic means of symmetric and asymmetric carbonyl stretching frequencies of 1,3-indanedione derivatives ($\bar{\nu}$) provide a general empirical correlation [Eq. (2)] with substituent constants $\Sigma X^{+}(R)$ in sense of the improved and extended Seth-Paul-Van Duyse equation [16]

$$\bar{\nu}(C=O) = 33.09\,\Sigma X^{+}(R) + 1\,610.64\,. \qquad (2)$$

To calculate the ΣX^{+} (R) values for compounds **1–4**, equations and substituent constants were taken from Refs. [15–19]. The ΣX^{+} (R) values for all investigated compounds **1–4** are listed in Table 1.

It follows from the differences between the experimental and calculated values ($\Delta\bar{\nu}$) that the carbonyl stretching frequencies of all compounds **1**, **3** and **4** fit excellently Eq. (2), which unambiguously assures 2-(1-acetoxyalkylidene)- and 2-(1-acetoxybenzylidene)-1,3-indanediones as the products of ketene acetylation of 2-acyl-1,3-indanediones. On the other hand, the carbonyl stretching frequencies of 2-acyl-1,3-indanediones (**2**) significantly deviate from the $\bar{\nu}(C=O)$ vs. ΣX^{+} (R) correlation of Eq. (2), the $\Delta\bar{\nu}$ values being 25.0–36.8 cm^{-1}. This indicates that the effects of substituents, because of intramolecular hydrogen bonding, are transmitted to the carbonyl groups markedly asymmetrically. The difference in the character of the carbonyl stretching doublet in series **2** and that of series **1**, **3** and **4** is well documented also by different regions of frequency separations $\Delta\nu = 54.5$–$61.6\,cm^{-1}$ and $\Delta\nu = 38.4$–$46.4\,cm^{-1}$. This can be regarded as a measure of the vibrational coupling. The significant substituent effect of group R^2 on the carbonyl stretching frequencies of the acetoxy group [the maximal difference between $\nu_{O1}(C=O)$ values being 12 cm^{-1}] eliminates the possibility that compounds **5** are formed by the acetylation of 2-acyl-1,3-indanediones. In above systems the substituent effects must be transmitted through the system of $-CO-C=C-O-$ grouping, which should markedly isolate the transmission.

The first overtones of carbonyl stretching frequencies $\nu_{O2}(C=O)$ of compounds **1** and **2** measured in CCl_4 solutions can be used to calculate the values of mechanical anharmonicities $\omega_e x_e$ according to

$$\omega_e x_e = [\nu_{O2}(C=O) - 2\,\nu_{O1}(C=O)]/2\,. \tag{3}$$

It is evident that the acetoxy group $C=O$ stretching vibration as well as the symmetric vibration of 1,3-dicarbonyl system of **1**, **2** and **4** exhibit negative values $\omega_e x_e = -13.0 - -54.9\,cm^{-1}$ and $\omega_e x_e = -2.1 - -27.4\,cm^{-1}$. On the other hand the mechanical anharmonicity values for the asymmetric mode of the $C=O$ stretching vibration are either positive or close to zero, $\omega_e x_e = -1.0 - +34.4\,cm^{-1}$, which according to [2–4] can be regarded as an evidence of a vibrationally coupled 1,3-dicarbonyl system in compounds **1** and **2**.

The structure of compounds **1a–1e** was investigated also using ^{1}H-NMR and ^{13}C-NMR spectra. The spectral data of **1a–1e** were compared with those of 1,3-indanedione and 3-acetoxy-2-indene-1-one, which structurally resemble compounds **1** and **5**. Structure **1** follows mainly from the similarity of signals of aromatic and carbonyl carbons with those of 1,3-indanedione as a model compound representing a typical 1,3-dicarbonyl system [5].

Optimal geometries of 2-(1-acetoxyethylidene)-1,3-indanedione (**1a**) and 2-acetyl-3-acetoxy-2-indene-1-one (**5**) ($R^2 = Me$) were obtained by a molecular mechanic method. The above geometries were used as an input for the quantum chemical CNDO/2 method. The results show that the total energy of 2-(1-acetoxyethylidene)-1,3-indanedione (**1a**) (calculated by CNDO/2 method) is by 60 kJ mol^{-1} lower than that of the alternative 2-acetyl-3-acetoxy-2-indene-1-one (**5**) ($R^2 = Me$). Also the value of steric energy (obtained by MMPI calculation) for compound **1a** is by 25 kJ mol^{-1} lower than that of **5** ($R^2 = Me$). Provided that the reaction is under thermodynamic control, this demonstrates that the ketene acetylation of 2-acyl-

1,3-indanediones (**2**) affords preferentially compounds **1**, which are more stable than compounds **5**. The results of MMPI calculations show that in 2-(1-acetoxy-alkylidene)-1,3-indanediones (**1a**–**1d**) the 2-(1-oxyalkylidene) moiety is coplanar with the plane of the 1,3-indanedione skeleton, the acetoxy group being nearly perpendicular to this plane. Deviations from the coplanarity and perpendicularity are maximally a few degrees. A higher negative charge on the oxygen atome of the acetoxy group of **1a** (following from CNDO/2 calculations) compared to **5** ($R^2 = Me$) indicates that in the reaction with ketene preferentially the enol-form **2** participates.

It can be concluded that besides of the NMR spectra the correlations for infrared spectral data, Eq. (1) and Eq. (2), as well as the mechanical anharmonicities defined by Eq. (3) appear to be useful tools of structure elucidation of cyclic 1,3-dicarbonyl compounds and may also be used in appropriate cases.

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