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On the Trimorphism of 7-Hydroxy-3-(*p*-methoxyphenyl)-4,6-dimethyl-1-indanone

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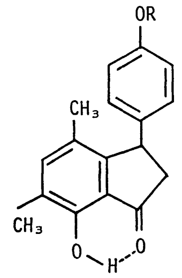
Synopsis. The reaction of 2′-hydroxy-4-methoxy-3′,5′-dimethylchalcone with anhydrous $AlCl_3$ in benzene gave three kinds of crystals having different melting points. It is concluded that the crystals are three modifications of 7-hydroxy-3-(*p*-methoxyphenyl)-4,6-dimethyl-1-indanone on the basis of their mutal transformations, IR spectra and X-ray analysis.

Although the transformation of chalcone into indanone using $AlCl_3$ has already been reported,[1] the indanone obtained by the present authors showed an interesting behavior-polymorphism. Thus, a brief report on the study is presented here.

The attempt to obtain 4,2′-dihydroxy-3′,5′-dimethylchalcone (**1**)[2] from the corresponding 4-methoxychalcone (**2**)[2] by demethylation with the aid of anhydrous $AlCl_3$ in benzene gave colorless needles (**3a**), mp 81—82 °C, colorless plates (**3b**), mp 87—88 °C, and colorless needles (**4**), mp 211—212 °C, besides a small amount of expected **1**.

Compound **3b** ($C_{18}H_{18}O_3$; $M^+=282$) produced the following UV spectrum (in methanol): 222 (log ε, 4.47), 261.5 (4.03), 286.5 (3.63) and 334 nm (3.26), suggesting the presence of substituted aromatic carbonyl. The NMR spectrum (in CCl_4) of **3b** showed signals due to two methyls ($\delta=1.77$s and 2.13s), one methoxyl ($\delta=3.66$s), five aromatic hydrogens ($\delta=6.64$d, 6.83d each $J=9$ Hz and $\delta=6.97$ s) and one hydroxyl ($\delta=9.09$ s). The signals ($\delta=2.36$ dd, $J=2$ and 18 Hz, $\delta=3.04$ dd, $J=8$ and 18 Hz, and $\delta=4.29$ dd, $J=2$ and 8 Hz) could be assigned to the $-COCH_2CH=$ group. The IR spectral data are shown in Table 1. All of these results indicate that **3b** is 7-hydroxy-3-(*p*-methoxyphenyl)-4,6-dimethyl-1-indanone with an intramolecular hydrogen bonding between the hydroxyl and the carbonyl groups (Fig. 1).[3] Since dimethyl ether of **4** was identical with methyl ether of **3b**, **4** proved to be 7-hydroxy-3-(*p*-hydroxyphenyl)-4,6-dimethyl-1-indanone. This conclusion was also supported by the spectral data.

Both **3a** and **3b** transformed into colorless crystals (**3c**), mp 95—96 °C, upon heating near to their melting points followed by solidification. It was proved that the structures of **3a** ($C_{18}H_{18}O_3$) and **3c** ($C_{18}H_{18}O_3$) are identical with that of **3b** by the comparison of their spectra. After crystallizing **3b** as well as **3c** from a small excess of methanol or 75% acetone, metastable **3a** was first separated out and then transformed into **3b**. The modifications **3b** and **3c** remained unchanged on standing at room temperature for five years, but **3a** transformed very slowly into **3b**.



(**3**) $R=CH_3$
(**4**) $R=H$

Fig. 1.

TABLE 1. IR SPECTRA OF 3

Phase	3a		3b		3c	
	ν(OH) cm⁻¹	ν(CO) cm⁻¹	ν(OH) cm⁻¹	ν(CO) cm⁻¹	ν(OH) cm⁻¹	ν(CO) cm⁻¹
KBr	3350	1668	3310	1668	3360	1672
Nujol	3350	1671	3320	1677	3360	1678
In CCl_4 and CS_2	ν(OH) 3310, ν(CO) 1678 cm⁻¹					

The X-ray diffraction patterms of powdered samples of **3a**, **3b**, and **3c** were entirely different, as shown in Fig. 2. Analysis of the Weissenberg photographs indicated that crystals of both **3a** and **3b** belong to a monoclinic system, and that their lattice constants are $a=11.2$, $b=$

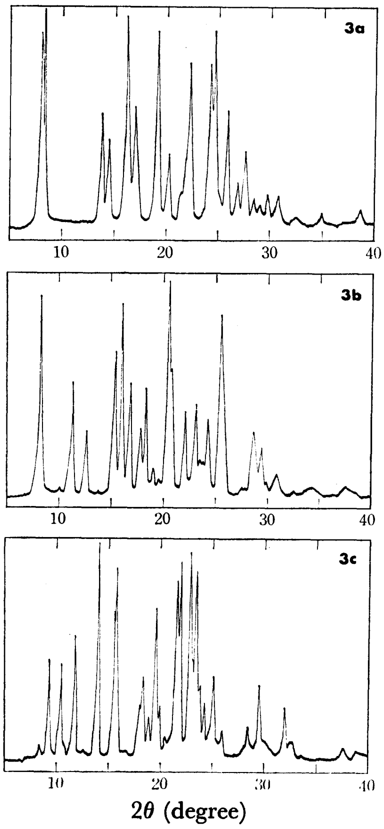


Fig. 2. X-Ray diffraction patterns of **3a**, **3b**, and **3c** by means of Ni filtered Cu*K*α radiation.

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Table 2. Derivatives of indanones (**3** and **4**)

Compound	Color and crystals	Molecular formula	Mp (°C)	Elementary analysis Found (%)	 Calcd (%)	Yield (%)
Methyl ether of **3** (Dimethyl ether of **4**)	Colorless plates	$C_{19}H_{20}O_3$	75—76	C 76.91 H 6.80	C 77.00 H 6.80	76[a)] (79)
Benzoate of **3**	Colorless plates	$C_{25}H_{22}O_4$	183—184	C 77.77 H 5.88	C 77.70 H 5.74	73[a)]
Oxime of **3**	Colorless needles	$C_{18}H_{19}NO_3$	151—152 (decomp)	N 4.75	N 4.71	80[a)]
2,4-DNPH of **3**	Red needles	$C_{24}H_{22}N_4O_6$	282—284 (decomp)	N 11.83	N 12.12	83[a)]
2,4-DNPH of **4**	Reddish orange needles	$C_{23}H_{20}N_4O_6$	285—287 (decomp)	N 12.61	N 12.50	85

a) These values show yields of the derivatives of **3b**. The yields of the derivatives of **3a** and **3c** are nearly the same as those of **3b**.

6.2, $c=10.2$ and $\beta=114°$ for **3a** and $a=10.7$, $b=15.6$, $c=9.3$ and $\beta=100°$ for **3b**. There is a small difference in the IR spectra of these three modifications in KBr and Nujol mull phases. The wave numbers of the absorption bands, ν(OH) and ν(CO), are shown in Table 1.

As mentioned above, it was found that the properties of **3a**, **3b**, and **3c** are different from each other in the solid state. However, the behavior of these modifications is identical in solution. They produced the same oxime, 2,4-DNPH, methyl ether and a benzoyl derivative; in two different solvent systems, their respective R_f values of tlc were the same and they produced identical UV and IR spectra (in CCl_4 and CS_2, Table 1).

Thus, it is concluded that **3a**, **3b**, and **3c** are three modifications of 7-hydroxy-3-(*p*-methoxyphenyl)-4,6-dimethyl-1-indanone.[4-6] The formation of these modifications might be due to differences in the packing mode of the molecule connected with hydrogen bonding in crystals.

Experimental

All melting points are uncorrected. The UV, IR and mass spectra were measured using Hitachi EPS-3T, JASCO IR-G (or DS-701G) and Hitachi RM-50GC spectrometers, respectively. The NMR spectra were recorded on a JEOL MH-100 spectrometer using TMS as an internal standard, and the X-ray analysis was carried out using a Rigakudenki Geigerflex D-2.

Indanone (3 and 4) and Chalcone (1). To a benzene solution of 5.0 g of **2**, 10 g of anhydrous $AlCl_3$ was added, and this suspension was kept at 50 °C for 2 h with stirring. The reaction mixture was hydrolyzed and then steam distilled. The black nonvolatile residue was dissolved in benzene, and to this solution, a 20% aqueous sodium hydroxide was added giving a yellow precipitate. a) From the precipitate; the precipitate was washed with benzene, then acetone and recrystallized from acetone with a small amount of methanol to give lemon yellow needles (**5**), mp about 240 °C (decomp). Compound **5** appeared to be a sodium salt of **3**, but was not further purified. A suspension of **5** in water was acidified, the precipitated white substance was collected and recrystallized from 75% acetone to give 0.61 g (12%) of **3b**. Modifications **3a** and **3c** were also obtained in the above manner. **3a**; Found: C, 76.53; H, 6.54%; mol wt (Rast), 282. **3b**; Found: C, 76.39; H, 6.24%; $M^+=282$. **3c**; Found: C, 76.63; H, 6.28%; $M^+=282$. Calcd for $C_{18}H_{18}O_3$ of **3a**, **3b**, and **3c**: C, 76.58; H, 6.43%; mol wt, 282.3. The R_f values of tlc on polyamide (Merck) were the same, 0.53 (Me_2CO: H_2O 3: 1) and 0.86 (*n*-BuOH: AcOH: H_2O 4: 1: 2) for **3a**, **3b** and **3c**. b) From the filtrate obtained by filtering off **5**; water was added to this filtrate, a benzene layer was taken off, and the precipitate which was produced by passing CO_2 into this sodium hydroxide solution was treated with acetic acid. The insoluble substance was recrystallized from ethanol to give 0.090 g (1.8%) of **4**. Found: C, 76.11; H, 6.08%; $M^+=268$. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%; mol wt, 268.3. NMR (in $CDCl_3$): $\delta=1.87$s and 2.14s (2 CH_3), $\delta=2.55$dd, $J=3$ and 20 Hz, $\delta=3.29$dd, $J=8$ and 20 Hz, $\delta=4.47$dd, $J=3$ and 8 Hz ($-COCH_2CH=$), $\delta=4.87$s and 9.30s (2 OH), $\delta=6.77$d and 6.97d, each $J=8$ Hz and $\delta=7.19$s (aromatic 5H). IR: ν (KBr), 3460, 3330 (2OH) and 1667 cm^{-1} (CO). Compound **4** was also obtained in a 16% yield by refluxing **2** with anhyhydrous $AlCl_3$ in benzene for 2 hr. The acetic acid solution from which **4** was filtered off was diluted with water. A yellow precipitate was produced and recrystallized from a mixture of benzene and ethanol to give 0.10 g (2.2%) of **1** in the form of orange prisms, mp 190—191 °C. This compound had no mixed melting point decrease with authentic chalcone.[2]

Derivatives from 3a, 3b, and 3c (melthyl ethers, benzoates, oximes and 2,4-DNPH) and from 4 (dimethyl ether and 2,4-DNPH). They were prepared by the usual methods. No pairs of methyl ethers and dimethyl ether, of benzoates and of oximes produced mixed melting point depressions, and the IR spectra and melting points of each derivative from **3a**, **3b**, and **3c** were identical to each other. The NMR spectrum of the methyl ether of **3** showed the presence of two methoxyls ($\delta=3.73$s and 3.93s), and its MW was found to be 296 (Rast). Other properties of these derivatives are shown in Table 2.

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