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Abstract

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2-PHENYL-4,5,6,7-TETRAHYDROINDANDIONE-1,3

Continuing the study of the relationship between structure and properties in the indandione-1,3 series, we recently reported investigations of the prototype of the indandione system—cyclopentene-4-dione-1,3 ([1,2]). The present work is devoted to a new analogue of indandione-1,3, namely, 2-phenyl-4,5,6,7-tetrahydroindandione-1,3 (I).

This compound had already been obtained in 1935 by Berlingozzi and Senatori ([3]), but they did not study it more closely and assigned to it an incorrect structure. We obtained I by a method analogous to that used for the synthesis of 2-arylindandiones-1,3, namely, by thermal condensation of $\Delta^{1,2}$-tetrahydrophthalic anhydride (III) with phenylacetic acid, obtaining the corresponding benzal-tetrahydrophthalide (II), which was rearranged with sodium methylate into 2-phenyl-4,5,6,7-tetrahydroindandione-1,3 (I). II is also obtained by condensation of $\Delta^{2,3}$-tetrahydrophthalic anhydride (IV) with phenylacetic acid, and here, evidently, the long-known thermal isomerization of IV into III first takes place ([4,5]). This circumstance was not taken into account by Berlingozzi and Senatori, who carried out the condensation precisely with IV ([3,6]) and thus arrived at an incorrect conclusion concerning the position of the double bond both in II and in I.

$$\text{(IV)} \xrightarrow{t^\circ} \text{(III)} \xrightarrow[-H_2O;\ -CO_2]{+C_6H_5CH_2COOH} \text{(II)} \xrightarrow{CH_3ONa} \text{(I)}$$

2-Phenyl-4,5,6,7-tetrahydroindandione-1,3 (I) is a light-yellow substance, dissolves in alkalis with a dark-violet coloration; it gives a colorless dioxime. Owing to the stability of I toward bases, we were able readily to carry out alkylation reactions of it in an alkaline medium, which was impossible with cyclopentene-4-dione-1,3 ([1,2]). Heating I with an equivalent amount of sodium methylate and methyl iodide gave, in nearly quantitative yield, the 2-methyl derivative (V). This reaction proceeds smoothly also at room temperature and even on shaking I with methyl iodide in the presence of calcium oxide. Reduction of I with zinc in acetic acid or catalytic hydrogenation in the presence of Raney nickel gives 2-phenylhexahydroindandione-1,3 (VI). Along with VI, a thick oil was also isolated, evidently a product of further reduction.

$$\text{(VI)} \xleftarrow{+\text{H}} \text{(I)} \xrightarrow[\text{CH}_3\text{ONa}]{+\text{CH}_3\text{J}} \text{(V)}$$

The IR spectra of the compounds obtained were recorded (see Table 1). In the spectrum of I only normal carbonyl bands and a double-bond band were found. A similar spectrum was obtained for V. It is interesting to note that the carbonyl frequencies of I and V are appreciably lower than those found for 2-phenylindan-1,3-dione and 2-methyl-2-phenylindan-1,3-dione, which is a general regularity when an aromatic ring is replaced by a double bond. The similarity of the IR spectra of I and V, as well as the absence of absorption in the region of the stretching vibrations of O—H bonds, excludes the possibility of the existence of I in the enol form and confirms its diketone structure. In the spectra of solid I and V a weak band appears near 3400 cm^{-1}, which is evidently an overtone of the carbonyl vibrations, as in (1).

2-Phenylhexahydroindan-1,3-dione (VI), on the other hand, differs greatly from I both in chemical properties and in structure. The IR spectrum of VI is characteristic of completely enolized β-diketones and does not contain a single band that could be assigned to ν CO of the dicarbonyl form VI(7,8). At the same time, in the spectrum of solid VI a broad band is observed at 2640–2660 cm^{-1}, found for many enolized β-diketones with a strong hydrogen bond (for example, dimedone (9)). This confirms the existence of solid VI exclusively in a strongly associated enol form. It was likewise not possible to detect the existence of the dicarbonyl form of VI in a solution of dichloroethane with alcohol. Unfortunately, we were unable to study VI in a less polar solvent because of its poor solubility.

The IR spectra show that compounds of the cyclopentene-4-dione-1,3 (1) and 4,5,6,7-tetrahydroindan-1,3-dione systems, like indan-1,3-diones (10), are not tautomeric and exist exclusively in the dicarbonyl form. By contrast, cyclopentane-1,3-diones (2), hexahydroindan-1,3-diones (11), and $\Delta^{5,6}$-tetrahydroindan-1,3-diones (2) are tautomeric substances, with characteristic existence in the enol form (as in six-membered cyclic β-diketones).

To confirm the structure of II, the IR spectra of II and 3-benzalphthalide were recorded. In addition to the high frequency of the lactone carbonyl (12), two double-bond bands also appear in the spectrum of II. The higher of them (1660 cm^{-1}), also found in the spectrum of 3-benzalphthalide, evidently belongs to the vibrations of the exocyclic double bond; and the lower, observed only in the spectrum of II, to the vibrations of the endocyclic bond.

Experimental part

3-Benzal-4,5,6,7-tetrahydrophthalide (II). a) In a flask equipped with a thermometer and a descending tube for distillation of the water liberated in the reaction, 45 g of $\Delta^{1,2}$-tetrahydrophthalic anhydride (III) (13), 2.5 g of anhydrous sodium acetate, and 45 g of phenylacetic acid are heated on a metal bath first to 180°, then gradually to 200° (in the flask). During the reaction, two additional portions totaling 2.5 g of sodium acetate are added. When about half of the calculated amount of water has distilled off, the temperature is gradually raised to 210°. After the calculated amount of water has been evolved (about 5.5 ml), the orange-red mass is cooled to 100–110°, poured into 200 ml of methanol, and left overnight in a refrigerator. The orange-yellow crystals are washed with a small amount of cold methanol. Yield 30.5 g (46%) of crude II, quite suitable for obtaining I. A little more material was isolated from the filtrate, so that the total yield increases to 55%. Mp 117°.

b) Similarly, from 0.43 g of $\Delta^{2,3}$-tetrahydrophthalic anhydride (IV) (5), 0.5 g of phenylacetic acid, and 0.1 g of anhydrous sodium acetate, by heating at 180–190° for 20 min, the same product II was obtained. Mp 117–118°. For purification, crude II is shaken with a warm dilute solution of sodium methylate, and the residue is crystallized from methanol or petroleum ether.

White crystals, m.p. 118°.

Found, %: C 79.72; H 6.30
$C_{15}H_{14}O_2$. Calculated, %: C 79.64; H 6.23

Dioxime was obtained from 0.5 g of substance I, 0.4 g of $NH_2OH \cdot HCl$, and 0.5 g of CH_3COONa in dilute methanol. White crystals, 0.25 g, m.p. 260° (from methanol).

Found, %: N 11.01
$C_{15}H_{16}O_2N_2$. Calculated, %: N 10.93

2-Methyl-2-phenyl-4,5,6,7-tetrahydroindandione-1,3 (V). 3 g of I are boiled for 3 h in 50 ml of methanol with sodium methylate (from 0.31 g of sodium) and 1.2 ml of CH_3I. After only a few minutes the dark-violet color of the solution changes to orange. The cooled solution is poured into water and left in a refrigerator. The crystals that separate (3 g; 94%) are recrystallized from methanol (or CH_3OH + water). Yellow crystals, m.p. 94–95°.

Found, %: C 80.29; H 7.00
$C_{16}H_{16}O_2$. Calculated, %: C 79.98; H 6.71

2-Phenylhexahydroindandione-1,3 (VI). a) 1.5 g of I in glacial acetic acid are heated on a boiling water bath with zinc dust until the solution no longer gives a violet color with alkali (characteristic of I), and poured into water. The white precipitate crystall-

Table 1

Infrared absorption spectra

Compound	State of substance (solvent)	Benzene ring	$> C=C <$ and $> C=N-$	$> C=O$	Region 3000–3700 cm^{-1}
2-Phenyl-4,5,6,7-tetrahydroindandione-1,3 (I)	Solid	a	1633 (76)	1693 (91)1735 (48)	b, c
2-Phenyl-4,5,6,7-tetrahydroindandione-1,3 (I)	$CH_2ClCHCl4 \cdot 10^{-2}$ *M*	–	1638 (13)	1702 (82)1745 (18)	–
2-Methyl-2-phenyl-4,5,6,7-tetrahydroindandione-1,3 (V)	Solid	a	1635 (76)	1691 (100)1742 (64)	b
2-Methyl-2-phenyl-4,5,6,7-tetrahydroindandione-1,3 (V)	$CH_2ClCH_2Cl6 \cdot 10^{-2}$ *M*	–	1637 (12)	1695 (93)1740 (23)	–
2-Phenylindandione-1,3	Solid	1585 (42)1602 shoulder	–	1708 (68)1740 (40)	–
2-Phenylindandione-1,3	$CHCl_3$ (13)	–	–	17121748	–
2-Methyl-2-phenylindandione-1,3	Solid (14)	1596 (68)	–	1710 (91)1747 (58)	–
Dioxime of 2-phenyl-4,5,6,7-tetrahydroindandione-1,3	Solid	1608 (54)	1651 (57)	–	$ 3065(62) < *br* > $3170 (55)
3-Benzal-4,5,6,7-tetrahydrophthalide (II)	Solid	a	1635 (75)1660 (76)	1756 (97)	–

Compound	State of substance (solvent)	Benzene ring	$>C=C<$ and $>C=N-$	$>C=O$	Region 3000-3700 cm^{-1}
3-Benzalphthalide	Solid	1608 (43)	1660 (46)	1778 (84)	—
2-Phenylhexahydroindandione-1,3 (VI)	Solid	1575 (80) shoulder;1600 (44);	1584 (85);1631 (62);	1611 (68);1661 (43)1679 (42)	2640-2660 (65) c
2-Phenylhexahydroindandione-1,3 (VI)	CH_2ClCH_2Cl +10% C_2H_5OH $4\cdot 10^{-2}$ *M*	1600 (44);	1631 (62);	1679 (42)	d

Note. a —weak band near 1600 cm^{-1}; b —weak band near 3400 cm^{-1}; c —recorded in the interval 2500-3700 cm^{-1}; d —because of solvent absorption this interval was not accessible.

All spectra were recorded on a single-beam IKS-12 instrument with a NaCl prism, in most cases in the intervals 1500-1760 and 3000-3700 cm^{-1}. Spectra of solid substances were obtained in paraffin oil. The band values are given in reciprocal centimeters; in parentheses is their relative intensity in absorption percent.

crystallized from dilute alcohol or hexane ether. Yield 0.3 g (20%), m.p. 229-230° (from $CHCl_3$).

b) 0.1 g of I in alcoholic solution is hydrogenated in the presence of Raney nickel and a small amount of KJ. The alcohol is distilled off in vacuo and the residue is crystallized from $CHCl_3$. M.p. 229°; with the product obtained by method a), it gives no depression of the melting point.

Found, %: C 78.79; H 7.23
$C_{15}H_{16}O_2$. Calculated, %: C 78.94; H 7.06

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Note: Figure translations are in progress. See original paper for figures.

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