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Abstract

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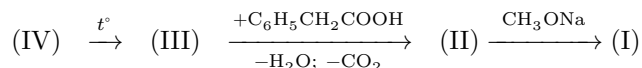
CHEMISTRY

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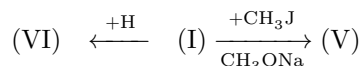
2-PHENYL-4,5,6,7-TETRAHYDROINDANDIONE-1,3

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.



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.



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 $2640\text{--}2660\text{ cm}^{-1}$, 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) | $CH_2ClCHCl_4$ $10^{-2} M$ | — | 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) | $CH_2ClCH_2Cl_6$ $10^{-2} M$ | — | 1637 (12) | 1695 (93)1740 (23) | — |
| 2- Phenylindandione- 1,3 | Solid | 1585 (42)1602 shoulder | — | 1708 (68)1740 (40) | — |
| 2- Phenylindandione- 1,3 | $CHCl_3$ | — | — | 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) < <i>br</i> > \$3170 (55) |
| 3-Benzal- 4,5,6,7- tetrahydrophthalide (II) | Solid | a | 1635 (75)1660 (76) | 1756 (97) | — |

| Compound (solvent) | State of substance | Benzene ring | > C=C < and > C=N- | > C=O | Region 3000-3700 cm ⁻¹ |
|--------------------------------------|--|--------------|-----------------------|---------------------------------|-----------------------------------|
| 3-Benzaldehyde | Solid | 1608 (43) | 1660 (46) | 1778 (84) | — |
| 2-Phenylhexahydroindandione-1,3 (VI) | Solid | 1575 (80) | 1584 (85); 1631 (62); | 1611 (68); 1661 (43); 1679 (42) | 2640-2660 (65) c |
| 2-Phenylhexahydroindandione-1,3 (VI) | CH ₂ ClCH ₂ Cl C ₂ H ₅ OH 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 CHCl₃).

- 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 CHCl₃. 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

C₁₅H₁₆O₂. Calculated, %: C 78.94; H 7.06

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