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Abstract

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SULFONATION OF 2-VERATRYL- AND 2-PIPERONYLINDANDIONES-1,3

Continuing the work (1,2) on the sulfonation of 2-monosubstituted indandiones-1,3, we have carried out the sulfonation of 2-veratryl- and 2-piperonylindandiones-1,3 (Ia, b), which led, together with the expected 2-veratryl- and 2-piperonylindandione-1,3-sulfo-2-acids (IIa, b), to the formation of bright-red cyclic enol sulfonates—sultones (IIIa, b).

Sulfonation was carried out by methods known for cyclic β-diketones (1,3,4): with dioxane sulfur trioxide ($D \cdot SO_3$), concentrated sulfuric acid in the presence of acetic anhydride, and chlorosulfonic acid in a solution of 1,2-dichloroethane. Irrespective of the sulfonating agent, sulfonic acids (IIa, b) and enol sulfonates (IIIa, b) are formed simultaneously.

(I) (II) (III)

For (I):

a) $R_1 = R_2 = OCH_3; \quad R_3 = H$

b) $R_1 R_2 = \begin{smallmatrix}-O\\-O\end{smallmatrix}\!> CH_2; \quad R_3 = H$

c) $R_1 = R_2 = OCH_3; \quad R_3 = SO_3H$

d) $R_1 R_2 = \begin{smallmatrix}-O\\-O\end{smallmatrix}\!> CH_2; \quad R_3 = SO_3H$

For (II):

a) $R_1 = R_2 = OCH_3$

b) $R_1 R_2 = \begin{smallmatrix}-O\\-O\end{smallmatrix}\!> CH_2$

For (III):

$$\text{a) } R_1 = R_2 = OCH_3$$

$$\text{b) } R_1R_2 = {}^{-O}_{-O}\!\!> CH_2$$

In sulfonation with concentrated sulfuric acid in the presence of acetic anhydride, a strong dependence is observed of the quantitative ratios of sulfonation products II and III on the duration of the experiment: if water is added to the reaction mixture after 3-5 min, the yield of IIa or IIb is 30-40%, and that of IIIa or IIIb is 25-30%; increasing the duration of the experiment leads to an increase in the yield of sulfonates (III) to 70%, while the yield of II is then negligible. In sulfonation with chlorosulfonic acid or $D \cdot SO_3$, enol sulfonates (III) invariably strongly predominate in the reaction products, and the yield of II is not above 5%.

The acids (IIa, b) were not isolated in the free state; their sodium salts crystallize well from dilute alcohol. The sulfo group in position 2 is firmly bound and is replaced under the action of bromine. The presence of the sulfo group at the second carbon atom is confirmed by UV and IR absorption spectra*. It is known (^{5}) that the diketone form of β-diketo—

* UV absorption spectra were recorded on an SF-4 instrument in methanol solution. IR spectra were recorded on an IKS-12 instrument in a suspension in paraffin oil or in 1,2-dichloroethane solution.

···of the indandione-1,3 series is characterized by intense absorption in the interval 220-240 mμ, which is also observed for compounds IIa, b (Fig. 1).

The carbonyl-group frequencies at 1703 and 1741 cm^{-1} (IIa) and 1705 cm^{-1} and 1746 cm^{-1} for compound IIb in the IR spectrum also correspond to the diketone form. Acids IIa and IIb were characterized in the form of their benzylthiuronium salts.

It is known (^{1,2}) that chlorosulfonic acid readily sulfonates the phenyl radical of 2-phenylindandione-1,3 in the para position. In the case of 2-veratryl- and 2-piperonylindandiones-1,3, sulfonation of the radical is facilitated by the presence of electron-donor substituents, and this is achieved even with a mixture of conc. sulfuric acid and acetic anhydride or $\mathrm{D \cdot SO_3}$ in the sterically less hindered *o*-position. Thereafter, apparently, interaction of the acid formed with the enol form of the diketone takes place. The molecular weight of compounds (IIIa, b) shows that such interaction proceeds intramolecularly. Of the three possible isomers of sulfonation of the veratryl or piperonyl nucleus, we consider the most probable to be isomer IIIv or IIIg, the formation of which is sterically less hindered.

Fig. 1. Ultraviolet absorption spectra in methanol: 1—IIIa, 2—IIb, 3—IIa, 4—IIIb

Compounds IIIa and IIIb are insoluble in alkali and in alcoholic alcoholate

Fig. 1. Ultraviolet absorption spectra in methanol: 1—IIIa, 2—IIb, 3—IIa, 4—IIIb

Figure 1: Fig. 1. Ultraviolet absorption spectra in methanol: 1—IIIa, 2—IIb, 3—IIa, 4—IIIb

solution. With alcoholic alkali the sultone-ether grouping is cleaved with formation of 2-monosubstituted indandiones-1,3 containing a sulfo group in the veratryl (piperonyl) radical (Iv, g). The free hydrogen atom at the second carbon is proved chemically: in alkali, compounds (Iv, g) dissolve with formation of a red solution and, in contrast to IIIa and IIIb, are readily brominated. In the bromination products Br is positively polarized, which is characteristic of 2-bromoindandiones-1,3 (1).

Table 1

Substance	State of substance	Characteristic frequencies in the range 1500-1800 cm^{-1} *
2-Veratrylindandione-1,3 (Ia)	Solid	1519 (83), 1590 (69), 1701 (88), 1741 (50)
2-Veratrylindandione-1,3 (Ia)	In dichloroethane	1715 ($\varepsilon = 1200$), 1749 ($\varepsilon = 380$)
1-Piperonylindandione-1,3 (Ib)	Solid	1506 (61), 1578 (38), 1601 (38), 1702 (85), 1744 (42)
1-Piperonylindandione-1,3 (Ib)	In dichloroethane	1715 ($\varepsilon = 980$), 1751 ($\varepsilon = 250$)
Veratrylindandione sulfonate (IIIa)	Solid	1520 (100), 1604 (79), 1635 (60), 1713 (82)
Veratrylindandione sulfonate (IIIa)	In dichloroethane	1717 ($\varepsilon = 580$)
Piperonylindandione sulfonate (IIIb)	Solid	1512 (66), 1584 (55), 1628 (55), 1628 (55), 1720 (75)
Piperonylindandione sulfonate (IIIb)	In dichloroethane	1719 ($\varepsilon =\sim 400$)
Methyl ether of 2-phenylindandione-1,3	Solid	1580 (80), 1630 (70), 1690 (75)
Methyl ether of 2-phenylindandione-1,3	In dichloroethane	1711 ($\varepsilon = 400$)

* For solutions in dichloroethane—only the carbonyl-group region.

The structure of the intramolecular enolic sulfonates (IIIa, IIIb) is also confirmed by the data of the IR and UV absorption spectra. In the ultraviolet region, the compounds (IIIa, IIIb) absorb at 240-250 mμ, which is characteristic [5] of the enolic configuration of indandiones-1,3 (Fig. 1).

The IR spectral data are presented in Table 1; their correct interpretation requires special explanation. The data available to date on the characteristic frequencies of indandione-1,3 derivatives [5] show that the dicarbonyl form is characterized by two absorption maxima: a very intense one at 1700-1720 cm^{-1} and a weak one at 1730-1760 cm^{-1}. Formation of derivatives of the enolic forms changes the first frequency of the carbonyl group only very slightly, while the second disappears. Consequently, from shifts of the carbonyl frequencies in indandione systems one cannot judge with complete certainty the diketone and enolic structures. It turns out, however, that these structures are readily distinguished on the basis of absorption intensity. If the diketone form is characterized by an intensity $\varepsilon = 800$-1200, then the enolic derivatives are characterized by $\varepsilon = 400$-600. In addition, the presence of an enolic configuration can be judged from the weak absorption in the region 1625-1635 cm^{-1}, presumably assigned to a double bond.

The simple route found for the synthesis of unusual condensed polycyclic sultones (IIIa and IIIb), and the method for spectroscopically distinguishing diketone and enolic structures in the indandione-1,3 series, may be of considerable interest in the chemistry of β-dicarbonyl compounds.

Experimental Part

Sulfonation of 2-veratryl- and 2-piperonylindandiones-1,3 with a mixture of sulfuric acid and acetic anhydride

To 2.83 g of Ia (2.66 g of Ib) in 25 ml of 1,2-dichloroethane is added a mixture of 1.1 ml of sulfuric acid and 6 ml of acetic anhydride in 10 ml of 1,2-dichloroethane. After 5-10 min, an orange crystalline precipitate begins to separate from the dark-red transparent mixture. After 1 hour, the solidified mass is treated with 50 ml of water; the undissolved precipitate is filtered off, and the aqueous layer is separated from the 1,2-dichloroethane layer. The aqueous layer is neutralized with sodium carbonate and saturated with sodium chloride. From the solution, 0.2 g (~5%) of the sodium salt IIa separates (respectively 0.5 g of IIb). It is crystallized from dilute alcohol and dried at 110°. White prisms. Soluble in water; insoluble in organic solvents; dissolves in alkali without coloration.

IIa Found, %: S 8.09. $C_{17}H_{13}O_7SNa$. Calculated, %: S 8.34
IIb Found, %: S 8.45. $C_{16}H_9O_7SNa$. Calculated, %: S 8.71

The benzylthiuronium salts of IIa and IIb were obtained by mixing aqueous solutions of the sodium salts IIa and IIb with an aqueous solution of benzylthiuronium chloride. The benzylthiuronium salt of IIa—white prisms (from alcohol). M.p. 201°.

Found, %: N 5.42; S 12.01
$C_{25}H_{24}O_7N_2S_2$. Calculated, %: N 5.30; S 12.13

The benzylthiuronium salt of IIb—white prisms (from alcohol). M.p. 200°.

Found, %: N 5.46; S 12.33
$C_{24}H_{20}O_7N_2S_2$. Calculated, %: N 5.47; S 12.51

The orange precipitate IIIa (IIIb) is crystallized from 200 ml of acetic acid. Yield: 2.1 g of IIIa (respectively 2 g of IIIb). IIIa—orange, felt-like crystals. Sparingly soluble in chloroform and benzene; insoluble in alcohol, acetone, water, and alkali. M.p. 251°. Molecular weight (by Rast) 320-330. Calculated 344.3.

Found, %: S 9.06
$C_{17}H_{12}O_6S$. Calculated, %: S 9.31

III —bright-red crystals. Solubility as for IIIa. M.p. 257°.

Found, %: S 9.45; 9.49
$C_{16}H_8O_6S$. Calculated, %: S 9.77

Sulfonation of Ia and Ib with chlorosulfonic acid or $D \cdot SO_3$ is carried out analogously to sulfonation with sulfuric acid. For 1 mole of the dione (Ia, b), 2-3 moles of sulfonating agent are used. The yield of IIa (IIb) is insignificant; that of IIIa (IIIb) is 60-70%.

Cleavage of IIIa with alcoholic alkali. A mixture of 3.44 g of IIIa, 80 ml of alcohol, and 4 g of finely powdered caustic soda is boiled for 1 hour on a water bath with a reflux condenser. A transparent red solution is formed. The alcohol is distilled off; the residue is dissolved in 40 ml of water, acidified with hydrochloric acid, and saturated with sodium chloride. A yellow precipitate of the sodium salt Ib separates. It is crystallized from 96% alcohol.

Found, %: S 8.52
$C_{17}H_{13}O_7SNa$. Calculated, %: S 8.71

Bromination of Ib is carried out in aqueous solution with bromine. The bromination product is salted out with sodium chloride and crystallized from diluted alcohol. The bromo derivative liberates iodine from an acidic solution of potassium iodide.

Found, %: Br 17.03; S 7.05
$C_{17}H_{12}O_7BrSNa$. Calculated, %: Br 17.25; S 6.92

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