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Abstract

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CHEMISTRY

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2-ETHYLENIMINO-2-ANISYLINDANDIONE-1,3

Many 2-aminoindandiones possess a clearly pronounced physiological action with low toxicity ([1]). Continuing systematic investigations in the series of amino derivatives of indandione, we set ourselves the goal of synthesizing the ethylenimino derivative of 2-anisylindandione and studying its properties. 2-Ethylenimino-2-anisylindandione-1,3 (I) was obtained by the interaction of 2-bromo-2-anisylindandione with ethylenimine in the presence of triethylamine as an acceptor of the hydrogen bromide evolved

$$\text{2-bromo-2-anisylindandione} + \mathrm{HN(CH_2CH_2)} + \mathrm{N(C_2H_5)_2} \longrightarrow \text{2-ethylenimino-2-anisylindandione } (I) - (C_2H_5)_3N \cdot HBr$$

After removal of triethylamine hydrobromide and evaporation of the ether–dioxane solution in vacuo, 2-ethylenimino-2-anisylindandione-1,3 was obtained as a colorless or slightly yellow substance. Investigation of its chemical properties showed that 2-ethylenimino-2-anisylindandione resembles the previously synthesized 2-ethylenimino derivative of 2-phenylindandione ([2]).

If a solution of 2-ethylenimino-2-anisylindandione-1,3 in absolute ether is saturated with dry hydrogen chloride, a white salt-like precipitate of the hydrochloride salt of 2-β-chloroethylamino-2-anisylindandione immediately separates. The reaction proceeds analogously also with hydrogen bromide and hydroiodic acid.

$$I \xrightarrow{\mathrm{HCl(HBr,\ HI)}} \mathrm{C_6H_4}\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\mathrm{C\,(C_6H_4OCH_3)\,NHCH_2CH_2Cl(J,\ Br)\cdot HCl(HBr,\ HI)}$$

$$(II)$$

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$$(II) \xrightarrow{Na_2CO_3} \begin{matrix} C_6H_4 \\ CO \quad CO \end{matrix} C\,(C_6H_4OCH_3)\,NHCH_2CH_2Cl(Br,\ J)$$

$$(III)$$

The salts dissolve in water, but the aqueous solutions are readily hydrolyzed with liberation of the free bases III. These bases can be obtained from the corresponding salts by treating them with a solution of soda. The 2-β-haloethylamino-2-anisylindandiones prove to be yellow crystalline substances, readily soluble in organic solvents.

If a solution of the salts or bases of 2-β-haloethylamino-2-anisylindandiones in acetic acid is treated with sodium nitrite, then, after dilution with water, a white precipitate of 2-(N-nitroso-β-haloethylamino)-2-anisylindandiones-1,3 is obtained. By the action of a 1:1 mixture of acetic anhydride and acetyl chloride on the salts or bases of 2-β-haloethylamino-2-anisylindandiones-1,3, the corresponding N-acetyl derivatives are obtained.

The infrared absorption spectra of the products obtained, recorded for suspensions in paraffin oil on an IKS-12 apparatus, give two absorption maxima of the carbonyl groups at 1701—1720 and 1735—1760 cm^{-1}, which are characteristic of the indandione grouping ([3]).

It is very interesting that 2-ethyleneimino-2-anizylindandione gives elevated values for the valence vibrations of the carbonyl groups (1720 and 1745 cm^{-1}) in comparison with 2-piperidino-2-anizylindandione ([4]), for which $\nu_{C=O} = 1698$ and 1741 cm^{-1} were found.

Such an effect of the ethyleneimine ring may be explained by the presence of conjugation of the unshared electron pair of the nitrogen atom with the three-membered ring ([5]), which in turn hinders the intramolecular

$$\equiv \overset{\delta\oplus}{N} : \longrightarrow C = \overset{\delta\ominus}{O}$$

interaction found for 2-aminoindandiones-1,3 ([3]). Because of this, an increase in the valence vibrations of the carbonyl groups is observed.

Table 1

2-Ethyleneimino-2-anizylindandione-1,3 and products of its transformation

$$C_6H_4\left\langle \begin{matrix} CO \\ CO \end{matrix} \right\rangle C\left\langle \begin{matrix} C_6H_4OCH_3(n) \\ X \end{matrix} \right.$$

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X	Empirical formula	m.p., °C	Solvent for crystallization	Yield, %	N, % found	N, % calc.	$\nu_{C=O}$, cm^{-1}
$N < CH_2 < CH_2$	$C_{18}H_{15}O_3N$	80	Acetone	73	4,78	4,79	1720, 1745
$NHCH_2CO$	$C_{18}H_{16}ClO_3NCl$	200–201(decomp.)	Alcohol + ether	89	3,83	4,06	1716, 1760
$NHCH_2CO$	$C_{18}H_{16}BrO_3NBr$	197–198(decomp.)	Same	87	3,16	3,08	1717, 1754
$NHCH_2CO$	$C_{18}H_{16}JO_3NJ$	166–168(decomp.)	» »	70	2,55	2,36	1716, 1747
$NHCH_2CO$	$C_{18}H_{16}ClO_3NCl$	98	Alcohol	67	4,25	3,93	1701, 1735
$NHCH_2CO$	$C_{18}H_{16}BrO_3NBr$	106	»	83	3,75	3,51	1701, 1735
$NHCH_2CO$	$C_{18}H_{16}O_3NJ$	110	»	89	3,33	3,16	1701, 1735
$N(NO)CH_2CO$	$C_{18}H_{15}O_4N_2Cl$	129–130(decomp.)	»	62	7,81	7,76	1714, 1747
$N(NO)CH_2CO$	$C_{18}H_{15}O_4N_2Br$	126(decomp.)	»	67	6,95	7,12	1714, 1749
$N(COCH_3)CH_2CO$	$C_{20}H_{18}O_4NCl$	158	»	79	3,80	4,05	1650, 1714, 1753
$N(COCH_3)CH_2CO$	$C_{20}H_{18}O_4NBr$	173	»	74	3,37	3,48	1650, 1714, 1747
$N(COCH_3)CH_2CO$	$C_{20}H_{18}O_4NJ$	184–186(decomp.)	»	84	3,02	2,93	1650, 1714, 1749

Experimental Part

2-Ethyleneimino-2-anizylindandione (I). 10 g of 2-Br-2-anizylindandione-1,3 are dissolved in absolute dioxane, and to the solution, gradually with stirring, is added a mixture of ethyleneimine (1.6 ml) and triethylamine (4.0 ml) dissolved in absolute ether. On the next day, the precipitated triethylamine hydrobromide

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is separated, and the filtrate is evaporated in vacuo. The resulting slightly yellowish crystalline precipitate is washed with small portions of ether, and the residue is dissolved in acetone with boiling. By evaporating the filtered acetone solution in vacuo, 6.5 g (73%) of colorless or slightly yellowish crystalline 2-ethyleneimino-2-anizylindandione-1,3 are obtained. M.p. 80°.

Hydrochloride of 2-β-chloroethylamino-2-anizylindandione-1,3 (II). 0.5 g of 2-ethyleneimino-2-anizylindandione-1,3 is dissolved in absolute ether, and the solution is saturated with dry hydrogen chloride. The white precipitate obtained is recrystallized from alcohol with add-

with ether. This gives 0.55 g (89%) of colorless 2-β-chloroethylamino-2-anisilindandione-1,3 hydrochloride. M.p. 200–201° (decomp.). Sparingly soluble in alcohol, insoluble in ether and benzene. Aqueous solutions undergo hydrolysis.

Hydroiodide of 2-β-iodoethylamino-2-anisilindandione-1,3 (II). 2 g of 2-ethyleneimino-2-anisilindandione are dissolved in ether, or preferably in acetone, and shaken with concentrated hydroiodic acid. The precipitate is recrystallized from alcohol with addition of ether. This gives 2.6 g (70%) of the hydroiodide salt of 2-β-iodoethylamino-2-anisilindandione-1,3. Colorless crystals turn yellow on standing in air. M.p. 166–168° (decomp.).

2-β-Chloroethylamino-2-anisilindandione-1,3 (III). 5 g of the hydrochloride salt of 2-β-chloroethylamino-2-anisilindandione are treated with 5% sodium carbonate solution, and the base is extracted with ether. The ethereal extract is dried over anhydrous sodium sulfate and evaporated in vacuo. The resulting yellow precipitate is recrystallized from alcohol. Yield 3.1 g (67%). M.p. 98°.

2-(N-Nitroso-β-chloroethylamino)-2-anisilindandione-1,3. 0.5 g of 2-β-chloroethylamino-2-anisilindandione hydrochloride is dissolved in acetic acid and an excess of sodium nitrite is added to the solution. The solution is diluted with water. The precipitate is recrystallized from alcohol. This gives 0.3 g (62%) of the nitroso derivative. Colorless crystals. M.p. 129–130° (decomp.).

2-(N-Acetyl-β-chloroethylamino)-2-anisilindandione-1,3. 0.5 g of 2-β-chloroethylamino-2-anisilindandione hydrochloride is treated with 5 ml of a mixture of acetic anhydride and acetyl chloride (1:1) and boiled until the precipitate passes into solution. After cooling, the solution is poured onto ice, and the precipitate is recrystallized from alcohol. This gives 0.4 g (70%) of the acetyl derivative. Colorless crystalline substance. M.p. 157–158°.

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