PREPARATION OF 8-(5-OXOINDENO[3,2-b]-4-PYRIDYL)-1-NAPHTHOIC ACIDS

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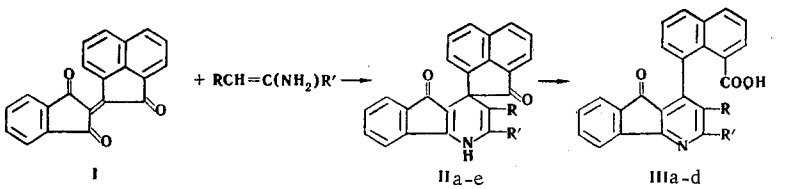
The condensation of 1-(1,3-indanedion-2-ylidene)-2-acenaphthenone with imines of β-dicarbonyl compounds gave 2,5'-dioxospiro{1,4'-acenaphthene-1',4'-dihydroindeno-[3,2-b]pyridines}. Oxidation of the pyridines with air oxygen at room temperature without catalysts brings about cleavage of the C–C bond to give 8-(5-oxoindeno[3,2-b]-4-pyridyl)-1-naphthoic acids.

8-(10,12-Dioxodiindeno[3,2-b:2',3'-e]-11-pyridyl)-1-naphthoyl chloride (dibepin) [1] is an analytical reagent for primary amines [2, 3]. The mechanism of this color reaction consists in reversible intramolecular cyclization of amides of 8-(10,12-dioxodiindeno[3,2-b:2',3'-e]-11-pyridyl)-1-naphthoic acid [4].

To extend the investigations of this phenomenon and to obtain acid chlorides that are dibepin analogs, we synthesized 8-(5-oxoindeno[3,2-b]-4-pyridyl)-1-naphthoic acids (IIIa-d). Their synthesis consists of two steps. The condensation of 1-(1,3-indanedion-2-ylidene)-2-acenaphthenone (I) with imino derivatives of β-dicarbonyl compounds gave 2,5'-dioxospiro[1,4'-acenaphthene-1',4'-dihydroindeno]3,2-b[pyridines] (IIa-e) [1]. These are stable, dark-red, crystalline substances with high melting points. They are characterized by extremely low solubility in both water and most organic solvents. Several methods of oxidation were tested for the conversion of II to naphthoic acids (III). The yields of III did not exceed 10% when the oxidation was performed with 30% hydrogen peroxide in alkaline media by the method in [6]. The oxidation with sodium nitrate in glacial acetic acid by the method used for 1,4-dihydropyridine [7] gave higher yields (up to 50%) of III. However, the most suitable method proved to be oxidation of II by means of air oxygen in alkaline media. In this case, acids III are formed in 66-80% yields. The reaction proceeds readily at room temperature and atmospheric pressure without catalysts when air is bubbled through the alkaline solution of II for 24 h.

To be certain that the cleavage of the C–C bond occurs under the influence of air oxygen and not as a result of alkaline hydrolysis with subsequent oxidation of the resulting 8-(5-oxo-1,4-dihydroindeno[3,2-b]-4-pyridyl)naphthoic acids, we studied the action of alcoholic alkali on II in the absence of oxygen (under argon). In this case, only the starting materials could be isolated from the reaction medium even after 3 days. Thus, in alkaline media, a proton is apparently initially split out, and an anion with an elevated electron density in the C–C bond is formed.



I IIa-e IIIa-d

a R=$CO_2C_2H_5$; b R=$COCH_3$; c R+R'=$COCH_2C(CH_3)_2CH_2$; d R=COC_6H_5; e R=CN; a, b, d, e R'=CH_3

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TABLE 1. 2,5'-Dioxospiro{1,4'-acenaphthene-1',4'-dihydroindeno-[3,2-b]pyridines} (IIa-e)

Compound	R	R'	mp, °C	λ_{max}, nm (lgε)*	Empirical formula	Found, %			Calc., %			Yield, %
						C	H	N	C	H	N	
IIa	$CO_2C_2H_5$	CH_3	240	218, 343, 480 (3,85; 3,08; 3,30)	$C_{27}H_{19}NO_4$	76,4	4,6	3,4	76,9	4,5	3,3	30
IIb	$COCH_3$	CH_3	290	218, 380, 480 (3,73; 3,55; 3,27)	$C_{26}H_{17}NO_3$	81,5	4,3	3,5	80,8	4,2	3,2	50
IIc	$COCH_2C(CH_3)_2CH_2$		250	218, 385, 480 (3,64; 4,0; 3,45)	$C_{29}H_{21}NO_3$	80,4	5,0	3,4	81,1	4,5	3,3	20
IId	COC_6H_5	CH_3	264	217, 320, 475 (3,81; 3,08; 3,25)	$C_{31}H_{19}NO_3$	81,9	4,4	3,1	82,1	4,2	3,3	55
IIe	CN	CH_3	270	217, 320, 480 (3,73; 3,41; 3,27)	$C_{25}H_{14}N_2O_2$	79,6	3,2	7,2	80,2	3,7	7,5	50

*In ethanol, 10^{-4} M.

TABLE 2. 8-(10,12-Dioxodiindeno[3,2-b:2',3'-e]-11-pyridyl)-1-naphthoic Acids (IIIa-d)

Compound	R	R'	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
IIIa	$CO_2C_2H_5$	CH_3	208	$C_{27}H_{19}NO_5$	73,6	4,0	4,0	74,1	4,3	3,2	80
IIIb	$COCH_3$	CH_3	209	$C_{26}H_{17}NO_4$	76,4	4,2	4,1	76,6	4,2	3,4	67
IIIc	$COCH_2C(CH_3)_2CH_2$		200	$C_{29}H_{21}NO_4$	77,8	4,6	3,6	77,7	4,2	3,2	80
IIId	COC_6H_5	CH_3	160	$C_{31}H_{19}NO_4$	78,5	4,3	2,9	79,3	4,1	2,9	66

Oxygen, acting as the oxidizing agent, attacks this bond and leads to its cleavage and the formation of the pyridine oxidation product (III).

EXPERIMENTAL

2,5'-Dioxo-2'-methyl-3'-acetylspiro{1,4'-acenaphthene-1',4'-dihydroindeno[3,2-b]pyridine} (IIb, Table 1). A 3 g (0.03 mole) sample of 2-amino-3-penten-4-one [9] was added to a solution of 1.5 g (0.05 mole) of 1-(1,3-indanedion-2-ylidene)-2-acenaphthenone [8] in 130 ml of glacial acetic acid at 100°C, and the mixture was heated for 3 h and cooled to give a light-brown precipitate. The precipitate was separated and crystallized from glacial acetic acid to give 1.9 g of IIb. The remaining II were similarly obtained (Table 1).

8-(2-Methyl-3-carbethoxy-5-oxoindeno[3,2-b]-4-pyridyl)-1-naphthoic Acid (IIIa, Table 2). A 0.7 g (1.5 mmole) sample of IIa was dissolved in 100 ml of 0.3 M NaOH in methanol, and carbon dioxide-free air was passed through the solution for 24 h. The solution was diluted with 200 ml of water and acidified to pH 3 with concentrated HCl. The resulting yellow precipitate was separated and reprecipitated from saturated $NaHCO_3$ solution. For further purification, IIIa was dissolved in hot dioxane, and an equal volume of water was added to the hot solution to give 0.5 g of light-yellow IIIa. The remaining III were similarly obtained (Table 2).

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