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G. Ya. DUBUR and Academician of the Latvian SSR G. Ya.
VANAG

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Abstract

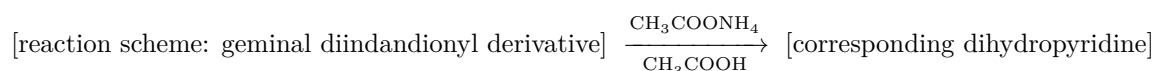
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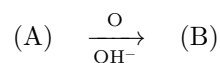
o-(2,3(CO),6,5(CO))-DIBENZOYLENISONICOTINOYL)-BENZOIC ACID

In previous works ^(1,2) we showed that geminal diindandionyl derivatives, under the action of ammonium acetate in glacial acetic acid, readily give the corresponding dihydropyridines:



It was of interest to use for this reaction the oxidation product of trisindandione (I)—oxytrisindandione (II) ^(3,4), which should give a 3-hydroxy-3,4-dihydropyridine derivative. The reaction of the enolic form of oxytrisindandione with ammonium acetate in glacial acetic acid proceeds readily and rapidly, with formation of a yellow crystalline substance which at ordinary temperature is practically insoluble in alkalis. On heating it dissolves somewhat in dilute alkalis and in sodium bicarbonate; upon addition of a more concentrated alkali solution, a salt precipitate separates. A series of salts was prepared in pure form. All of them are sparingly soluble in water.

The same salts can also be obtained by oxidation of indandione-1,3-spiro-(2:4')-2',3'(CO),6',5'(CO)-dibenzoylenedihydropyridine (III) with perhydrol in alcoholic medium in the presence of alkali. On acidification of these solutions, the same substance is isolated as that obtained by the action of ammonium acetate on oxytrisindandione. The ability of III to oxidize in alkaline medium to salt-like substances recalls the acenaphthene-1-spiro-(2:4')-2',3'(CO),6',5'(CO)-dibenzoylenedihydropyridine (A), studied by us earlier ⁽²⁾, which in alkaline medium is oxidized to 8-(2',3'(CO),6',5'(CO)-dibenzoylenepyridyl-4')-naphthoic-1-acid (B). It can therefore be assumed that III, upon oxidation in alkaline medium, gives salts of *o*-(2,3(CO), 6,5(CO)-dibenzoylenisonicotinoyl)-benzoic acid (IV). Upon acidification of solutions of these salts, acid IV itself is isolated. Characteristically, in analogy to acid B, acid IV is rather readily decarboxylated, which will be the subject of a separate communication.



Reaction scheme with compounds (I), (II), (III), (IV), and (V), showing transformations with O/OH^- , CH_3COONH_4/CH_3COOH , and $RONa$; for (V): a) $R = CH_3$, b) $R = C_2H_5$.

Figure 1: Reaction scheme with compounds (I), (II), (III), (IV), and (V), showing transformations with O/OH^- , CH_3COONH_4/CH_3COOH , and $RONa$; for (V): a) $R = CH_3$, b) $R = C_2H_5$.

The analogy between III and A also continues with respect to the reaction with sodium alcoholates, which cleave the five-membered indandione ring. It is interesting to note that, as in ⁽²⁾, in this case also no dihydropyridine derivatives were obtained, but instead pyridine derivatives—the esters of *o*-(2,3(CO),6,5(CO)-dibenzoylisonicotinoyl)benzoic acid (V)—were formed directly. The identical substance was also obtained from the silver salt of acid IV by the action of an alkyl halide on it. These esters (V) are very resistant to hydrolysis reactions.

At the same time, in accepting structure IV one must also accept the reaction scheme $II \rightarrow IV$, in which, in addition to cyclization, rupture of the five-membered indandione ring occurs.

It is necessary to note a certain difference in the behavior of III and A. Oxidation of III in alcoholic alkali in the presence of hydrogen peroxide proceeds very rapidly: already after one minute a yellow precipitate appears, whereas for A at room temperature tens of hours are required (the reaction rate depends to a considerable extent on the amount of water in the solution). Dihydropyridine III also reacts more rapidly with sodium alcoholates. Acid B dissolves well both in alkalis and in sodium bicarbonate, whereas acid IV, as already stated, is almost insoluble in them; it dissolves better in an aqueous-alcoholic mixture to which a small amount of alkali has been added.

The oxidation of dihydropyridine III was carried out by us earlier ⁽¹⁾, but a dimer structure was erroneously proposed for the product obtained.

Experimental Part

***o*-(2,3(CO),6,5(CO)-dibenzoylisonicotinoyl)benzoic acid (IV). a) From oxytriscindandione.** 8 g of the enol form of oxytriscindandione in 240 ml of glacial acetic acid and 24 g of ammonium acetate are boiled for 2 hours. After cooling, the precipitate is sepa-

are washed and boiled with 75 ml of acetic acid. There remain 5 g of a yellow crystalline substance, m.p. 365–368°.

b) **By oxidation of indandione-1,3-spiro-(2 : 4')-2',3'(CO), 6§' 5' §(CO)-dibenzoyldihydropyridine (III).** 2.15 g of III are suspended in 150 ml of methanol, 15 ml of 10% caustic soda and 10 ml of perhydrol are added. The red-brown precipitate dissolves with a green coloration, and after a few minutes a yellow precipitate of the sodium salt of acid IV

separates. The salt is dissolved in a water-alcohol mixture (1 : 1) by the addition of one drop of alkali, and acid IV, m.p. 364° (from dioxane), is precipitated by acidification. The yellow crystals do not dissolve in sodium bicarbonate. It melts without depression with the substance obtained according to a).

Found, %: N 3.45(a); 3.13(b)
 $C_{27}H_{13}O_5N$. Calculated, %: N 3.25

Sodium salt. 0.5 g of IV is dissolved with heating in 50 ml of a water-alcohol mixture to which 1 ml of 1% NaOH has been added, and the hot solution is filtered through a heated funnel. Fine yellow needles, m.p. 390° (dec.).

Found, %: N 3.39; Na 4.85
 $C_{27}H_{12}O_5NNa$. Calculated, %: N 3.09; Na 5.07

Potassium salt. 0.5 g of III is suspended in 40 ml of ethanol, 5 ml of 2% KOH and 3 ml of perhydrol are added. On the following day the yellow crystalline precipitate is separated, m.p. 360° (dec.). It dissolves in water and in dilute alcohol.

Found, %: N 2.76; K 8.06
 $C_{27}H_{12}O_5NK$. Calculated, %: N 2.98; K 8.33

Silver salt. To a hot solution of 0.1 g of the obtained potassium salt in 70 ml of dilute alcohol (1 : 1), an excess of $AgNO_3$ solution is slowly added. The yellow precipitate dissolves in hot solutions of $Na_2S_2O_3$ and dilute ammonia. The salt could not be purified.

Found, %: N 2.85; Ag 16.9
 $C_{27}H_{12}O_5NAg$. Calculated, %: N 2.60; Ag 20.1

Diethylamine salt. Analogously to the sodium or potassium salt in alcoholic solution. Yellow crystals (from dioxane), m.p. 340°.

Found, %: N 5.54
 $C_{31}H_{24}O_5N_2$. Calculated, %: N 5.55

Piperidine salt. Acid IV is boiled in ethanol with piperidine, and the precipitate is boiled with dioxane. Fine yellow needles remain, m.p. 326°.

Found, %: N 5.54
 $C_{32}H_{24}O_5N_2$. Calculated, %: N 5.42

β -Phenylisopropylamine salt. 0.2 g of III, 2 ml of β -phenylisopropylamine and 2 ml of perhydrol in 20 ml of methanol are boiled for 2 hours. Yellow crystals (from dioxane), m.p. 263°.

Found, %: N 4.97
 $C_{36}H_{26}O_5N_2$. Calculated, %: N 4.94

Acid chloride of acid IV. 5.8 g of thoroughly ground acid IV are boiled with 50 ml of thionyl chloride for 3 hours. The substance is converted into a yellow

finely crystalline precipitate of the acid chloride, m.p. 335°.

Found, %: N 3.08; Cl 7.90

$C_{27}H_{12}O_4NCl$. Calculated, %: N 3.11; Cl 7.88

Ethyl ester of acid IV. a) 0.1 g of the silver salt of acid IV and 6 ml of ethyl iodide are heated in a sealed ampoule for 6 h at 180°. After the ampoule is opened, the ethyl iodide is evaporated, the residue is treated with 2% ammonia and crystallized from glacial acetic acid, m.p. 325–327°.

b) 0.3 g of III and 25 ml of 1% sodium ethylate are left overnight. The yellow precipitate is crystallized twice from glacial acetic acid. Fine needles (Vb), m.p. 322–325°; a mixture with the ester prepared according to a) melts without depression.

Found, %: N 2.85(a); 2.92(b)

$C_{29}H_{17}O_5N$. Calculated, %: N 3.05

Methyl ester of acid IV. 0.3 g of III and 20 ml of 3% sodium methylate are boiled on a water bath for 10 min. The yellow precipitate (Va) is crystallized from glacial acetic acid, m.p. 338°.

Found, %: N 3.08

$C_{28}H_{15}O_5N$. Calculated, %: N 3.15

Institute of Organic Synthesis
Academy of Sciences of the Latvian SSR

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CITED LITERATURE

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

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