

## CONTRIBUTION TO THE STUDY OF CYCLOCONDENSATIONS OF CYANOACETIC ACID DERIVATIVES WITH BENZYLIDENEACETOPHENONE

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It was proved that reaction of cyanoacetamide with benzylideneacetophenone in an alkaline medium affords, in addition to 3-cyano-4,6-diphenyl-3,4-dihydro-2-pyridone (*I*), also 3-cyano-4,6-diphenyl-2-pyridone (*III*) which is formed by reduction of the starting unsaturated ketone with the dihydro derivative *I*. When the cyclocondensation is performed with a mixture of ethyl cyanoacetate and ammonium acetate instead of cyanoacetamide, this dehydrogenation of the primary product *I* takes place to a smaller extent.  $^1\text{H-NMR}$  spectra revealed that the compound *I* consists of *cis*- and *trans*-forms whereas the alkyl derivatives *V-VII* were isolated exclusively as the *cis*-isomers.

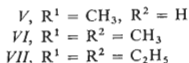
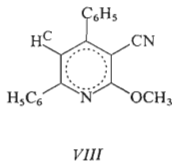
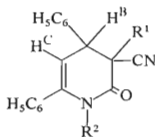
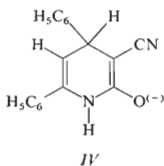
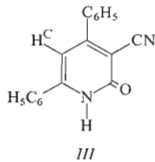
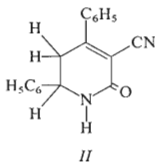
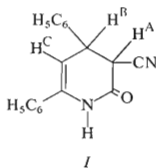
The cyclocondensation of functional derivatives of cyanoacetic acid with  $\alpha,\beta$ -unsaturated ketones and aldehydes represents one of the best ways leading to dihydro derivatives of 2-pyridone $^{1-9}$ . Within the framework of investigation of compounds with luminiscence properties we were interested in the product of this reaction with benzylideneacetophenone, *i.e.* 3-cyano-4,6-diphenyl-3,4-dihydro-2-pyridone (*I*), which according to the data in ref. $^{4-6,8}$  exhibits a blue fluorescence in the ultraviolet light. Contrary to the previous reports $^{4-6,9}$ , assuming an alternative structure *II*, Duburs and collaborators $^8$  have recently shown that the formula *I* fits better the interpretation of the IR and  $^1\text{H-NMR}$  spectra of this compound.

We reproduced both the alternative methods of preparation of the compounds *I*: reaction with cyanoacetamide and sodium ethoxide $^4$  and reaction with a mixture of ethyl cyanoacetate and ammonium acetate $^9$ . We found that the first method $^4$  afforded a product which exhibited a light blue fluorescence in the UV light and which was a mixture of the pyridone *III* and the corresponding 3,4-dihydro derivative *I*. Thin-layer chromatography of the reaction mixture has shown that the mentioned fluorescence was solely due to the compound *III*. In accord with this finding, the second method $^9$  afforded only the non-fluorescent dihydro derivative *I* beside traces of the compound *III*. The mixture of compounds *I* and *III* can be transformed into the fluorescent product *III* by oxidation with chromium trioxide $^8$  or nitrous acid $^2$ .

The formation of the pyridone derivative *III* in the cyclocondensations<sup>4,9</sup> can be explained by dehydrogenation of the dihydro compound *I* by part of the unreacted benzylideneacetophenone:



In accord with this assumption we proved  $\omega$ -phenylpropiophenone in the original reaction mixture after the cyclocondensation and, moreover, we accomplished the reaction (*A*) using solely the components required by this reaction. The transformation (*A*) proceeds best *via* the anion *IV* which is formed in the alkaline medium from the compound *I* by splitting off proton in the position 3. An information about the properties of the anion *IV* was obtained by <sup>1</sup>H-NMR spectroscopic study of a solution of the dihydropyridone *I* in a mixture of sodium perdeuteriomethoxide and perdeuteriomethanol. The <sup>1</sup>H-NMR spectrum exhibited, in addition to the multiplet of ten aromatic protons at  $\delta$  7.0–7.5, only a singlet of one proton at  $\delta$  4.38. From this one can infer that in the anion *IV*, beside the prototropic exchange  $NH \rightarrow ND$ , an exchange of the hydrogen atom in the position 4 for deuterium also takes place, probably by a radical or hydride mechanism. This can explain the fact that in the compound *I* this hydrogen atom is very reactive in an alkaline medium toward oxidation reagents. Thus, *e.g.* already boiling a solution of the compound *I* in aqueous dioxane in the presence of sodium hydroxide results in its almost complete conversion to the pyridone *III*, probably by the action of the atmospheric oxygen dissolved in the reaction medium.



The assumed formula of the anion *IV* is also in accord with our finding that alkylation of the dihydro compound *I* with methyl iodide and sodium hydride affords the non-fluorescent 3-methyl derivative *V* or, when an excess of alkylation reagents is used, the 1,3-dialkyl derivatives *VI* and *VII* which are also non-fluorescent. On the contrary, the pyridone *III* affords under identical conditions the O-methyl derivative *VIII* as the principal product<sup>12</sup>.

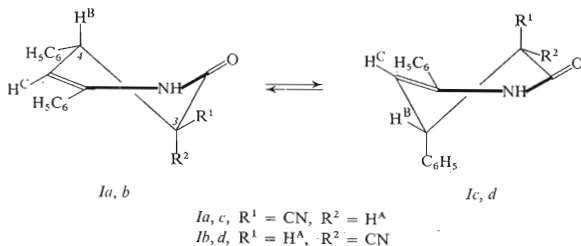
The alternative structures of the dihydro derivatives *I* and *II* differ particularly in that for the constitutional type *I* we must assume the existence of *cis-trans* isomerism. Duburs and coworkers<sup>8</sup> reported for the 60 MHz <sup>1</sup>H-NMR spectrum in addition to the signals of the NH and phenyl groups only three further signals of the heterocyclic protons without discussing in detail the character of the spin interaction between them. We investigated therefore the multiplicity of the signals of the protons H<sup>A</sup>, H<sup>B</sup> and H<sup>C</sup> in the 100 MHz spectrum of the compound *I* and proved in this way the existence of the two possible stereoisomers *Ia* and *Ib*, or *Ic* and *Id*. The character of the mentioned multiplets, together with the decoupling experiments, enabled us to determine the coupling constants  $J_{AB}$  and  $J_{BC}$  with sufficient accuracy and therefore to assign the particular signals to the protons H<sup>A</sup>, H<sup>B</sup> and H<sup>C</sup> (Table I). A study on models of the optimum geometry of the stereoisomers *Ia* and *Ib* shows that the advantageous conformation of the phenyl group in the position 4 is the pseudoequatorial one. In good accord with this, the coupling constant  $J_{BC}$  in both forms *Ia,b* varies less with the configuration ( $\Delta J = 3.7$  Hz) than the constant

TABLE I

<sup>1</sup>H-NMR Spectral Characteristics of the Studied Compounds (solutions in hexadeuteriodimethyl sulphoxide, 100 MHz, 37°C)

Compound	Chemical shifts $\delta$ , ppm <sup>a</sup>				Coupling constants, Hz	
	H <sup>A</sup>	H <sup>B</sup>	H <sup>C</sup>	H(N)	$J_{AB}$	$J_{BC}$
<i>Ia</i> <sup>b</sup>	4.62 d	4.37 dd	5.44 d	10.25	13.2	3.0
<i>Ib</i> <sup>b</sup>	4.78 d	4.13 dd	5.73 d	10.25	6.7	6.7
<i>III</i>	—	—	6.80 s	12.71	—	—
<i>V</i>	1.60 <sup>c</sup>	4.10 d	5.67 d	10.30	—	5.0
<i>VI</i>	1.56 <sup>c</sup>	4.00 d	5.56 d	2.93 <sup>c</sup>	—	5.0
<i>VII</i>	0.98 t <sup>d</sup>	3.98 d	5.47 d	1.14 t <sup>d</sup>	—	6.5
	1.8—2.4 m <sup>d</sup>			3.2—3.9 m <sup>d</sup>		

<sup>a</sup> All compounds exhibit also multiplets of the phenyl protons at  $\delta$  7.2—7.95 ppm; <sup>b</sup> Duburs and collaborators report<sup>8</sup> for H<sup>A</sup>, H<sup>B</sup> and H<sup>C</sup> in the compound *I* the values  $\delta$  4.10, 4.50 and 5.30 ppm, respectively; <sup>c</sup> singlet of the methyl group bonded in the same position; <sup>d</sup> signals of the ethyl group at the same position.



$J_{AB}$  which depends more on the relative configuration of the 3-cyano group and the 4-phenyl group ( $\Delta J = 7.3$  Hz). The value of  $J_{AB}$  can be directly taken as a function of torsion angles between the bonds  $C-H^A$  and  $C-H^B$  (projected along the  $C_{(4)}-C_{(3)}$  bond) according to the general Karplus relationship<sup>10,11</sup>  ${}^3J = A + B \cdot \cos \Phi + C \cos 2\Phi$ . The found values of  $J_{AB}$  are in a satisfactory agreement with the values estimated from molecular models (Table II); therefore the isomer with the greater value of  $J_{AB}$  has *trans*-configuration (*Ia*) whereas the isomer with the smaller  $J_{AB}$  value has *cis*-configuration (*Ib*). This assignment is supported also by the fact that in the compound *Ib*, in which there is *cis* relation between the phenyl and the cyano group and which at the same time has a pseudoequatorial phenyl group in the position 4, we can expect a smaller shielding of the olefinic proton caused by the magnetic anisotropy of the  $C\equiv N$  triple bond. In actual fact, the chemical shift of the  $H_C$  proton for the compound with the assigned configuration *Ib* is by 0.3 ppm greater than that for *Ia*. The comparison of the measured and estimated values

TABLE II

Values of Coupling Constants Calculated According to the Karplus Relationship<sup>10,11</sup> for Some Idealised Geometric Forms of the Compound *I*

Formula (isomer)	Torsion angles <sup>a</sup> , °		Coupling constants Hz	
	$\Phi_{AB}$	$\Phi_{BC}$	$J_{AB}$	$J_{BC}$
<i>Ia</i> ( <i>trans</i> )	180	100	13.0	2.5
<i>Ib</i> ( <i>cis</i> )	60	100	4.0	2.5
<i>Ic</i> ( <i>trans</i> )	65	20	3.4	9.9
<i>Id</i> ( <i>cis</i> )	55	20	4.7	9.9

<sup>a</sup> Measured on Dreiding models.

of  $J_{AB}$  and  $J_{BC}$  supports also the mentioned assumption of the pseudoequatorial orientation of the phenyl group in the position 4. For a pseudoaxial phenyl group the value of  $J_{BC}$  should be about 10 Hz (ref.<sup>10,11</sup>) and the constant  $J_{AB}$  should be about one half of this value. This is clearly at variance with the found values of these constants (Table I) which agree relatively well with the estimated values for a pseudo-equatorial phenyl.

Since the chemical shifts of the protons  $H^B$  and  $H^C$ , and the interaction constants  $J_{BC}$  for the alkyl derivatives *V–VII*, are similar to those found for the isomer *Ib*, we assign *cis*-configuration to these compounds. Certain differences between experimental and calculated values of  $J_{BC}$  (Tables I and II) can be caused either by the existence of a rapid conformational equilibrium of the type  $Ib \rightleftharpoons Id$  or by a too idealised geometry of the *cis*-isomers, used in the calculations. On the basis of the abovementioned considerations, it was possible to determine the composition of the mixture of pyridone derivatives, resulting from the studied cyclocondensation reactions of benzylideneacetophenone (Table III). We can derive from these data that, under the experimental conditions used, the *cis*  $\leftarrow$  *trans* isomerisation in the compound *I* is a spontaneous process. After crystallisation from acetic acid, the cyclocondensation product represented exclusively the isomer *Ia*. After some time its <sup>1</sup>H-NMR spectrum began to exhibit signals of the second form *Ib*, the integrated intensity of the signals  $H^A$ ,  $H^B$  and  $H^C$  of the both forms *Ia,b* being constant. It is highly probable that the *cis-trans* isomerisation proceeds by a prototropic mechanism,

TABLE III  
Percentages of the Products of Cyclocondensation Reactions of Benzylideneacetophenone  
Determined by <sup>1</sup>H-NMR Spectroscopy (37°C, hexadeuteriodimethyl sulphoxide).

Method of preparation	Ref.	% <i>Ia</i>	% <i>Ib</i>	% <i>III</i>
Cyanoacetamide and sodium ethoxide, fresh product	4	70	0	30
Cyanoacetamide and sodium ethoxide, after 14 days	4	39 <sup>a</sup>	32 <sup>a</sup>	29 <sup>a</sup>
Ethyl cyanoacetate and ammonium acetate, product after 14 days	9	56	37	7
Chromatographically purified compound <i>I</i>	this work	59	41	0

<sup>a</sup> Spectrophotometric measurement at the long-wavelength maximum of the compound *I* (367 nm, 20°C) showed 66% *Ia,b* and 34% *III*.

preferentially *via* the anion *IV*. The mentioned fact that the *cis*-isomers *V–VII* were isolated as exclusive products in the alkylation of the compound *I* indicates a marked stereospecificity of the reaction. The reason of this stereospecificity is probably that the phenyl group in the position 4 sterically hinders an axial attack at the position 3.

The absorption and emission curves of the electronic spectra of the pyridone *III* in methanol are compared in Fig. 1. It is evident that under conditions of the measurement the absorption band at 362 nm and the emission band at 435 nm are nearly mirror images of each other. This indicates a similar arrangement of the vibrational levels in the ground and in the first excited singlet states. On the contrary, under identical conditions of measurement (room temperature), the dihydropyridone *I* exhibits no emission electronic band. It is hence obvious that the luminiscence of the products of the cyclocondensation of cyanoacetic acid derivatives with benzylideneacetophenone is caused exclusively by the pyridone *III*. A revision is thus necessary of the previous data<sup>4,6,8</sup> concerning the fluorescence of the dihydro compound *I* under laboratory conditions.

TABLE IV  
IR and UV Spectral Data of the Studied Compounds

Compound	IR spectrum, nujol, cm <sup>-1</sup>				UV spectrum, ethanol, nm	
	$\nu(\text{NH})$	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{O})$	other	$\lambda_{\text{max}}(\epsilon \cdot 10^{-3})$	$\lambda_{\text{max}}(\epsilon \cdot 10^{-3})$
<i>I</i> <sup>a</sup>	~3 200 <sup>b</sup>	2 240 w	1 690 s	1 605 w <sup>a</sup>	202 (32.4) 222 (19.6)	274 (6.7)
<i>III</i> <sup>d</sup>	~3 000 <sup>b</sup>	2 219 m	—	1 640 s <sup>e</sup> 1 610 s <sup>c</sup>	202 (40.5) 257 (19.6)	283 (8.4) 367 (14.3)
<i>V</i>	~3 200 <sup>b</sup>	2 225 w	1 690 s	1 598 m <sup>c</sup>	202 (41.0) 224 (21.6)	275 (6.7)
<i>VI</i>	—	2 218 w	1 695 s	1 657 s <sup>c</sup> 1 600 m <sup>c</sup>	204 (30.1) 224 (15.1)	268 (4.8)
<i>VII</i>	—	2 240 w	1 670 s	1 598 m <sup>c</sup>	202 (25.8) 225 (12.0)	266 (3.5)
<i>VIII</i>	—	2 222 s	—	1 583 m <sup>c</sup> 1 575 <sup>c</sup> 1 545 <sup>c</sup>	205 (33.9)	258 (19.1) 326 (19.4)

<sup>a</sup> Ref.<sup>8</sup>: 3 223, 3 120, 2 263 and 1 695 cm<sup>-1</sup>; 203 (24.5), 225 (16.9), 277 (5.9) nm; <sup>b</sup> broad band due to association; <sup>c</sup>  $\nu(\text{C}=\text{C})_{\text{conj.}}$  and  $\nu(\text{C}=\text{C})_{\text{arom.}}$ ; <sup>d</sup> ref.<sup>8</sup>: 3 150, 3 035, 2 228 and 1 650 cm<sup>-1</sup>; 206 (17.5), 258 (13.5), 290 (5.3), 368 (10.2) nm; <sup>e</sup>  $\nu(\text{CONH})$  in the pyridine moiety.

## EXPERIMENTAL

The temperature data are uncorrected, the melting points were determined on a Boetius (GDR) block. Spectral measurements were performed on the following instruments:  $^1\text{H-NMR}$  spectra on a Varian XL-100 instrument (100 MHz, in hexadeuteriodimethylsulphoxide, tetramethylsilane as standard), IR spectra on a Perkin-Elmer 325 spectrophotometer (nujol), UV and VIS spectra on a Specord UV VIS (Zeiss, Jena) spectrophotometer (in ethanol) and on a fluorescence spectrophotometer Aminco-Bowman (methanol). Thin-layer chromatography was performed on Silufol R UV 254 adsorbent (Kavalier, Votice, ČSSR), the spots were detected by UV lamp and iodine vapours. The compounds *III* and *VIII* exhibit a blue fluorescence, the dihydro compounds *I*, *V*–*VII* quench the adsorbent emission.

## Reaction of Benzylideneacetophenone with Cyanoacetamide

Cyanoacetamide (23.9 g) was condensed with benzylideneacetophenone (59.2 g) in ethanol (100 ml) in the presence of sodium ethoxide (from 6.5 g of sodium and 80 ml of ethanol) according to ref.<sup>4</sup>. The precipitated products (82 g) were filtered and washed with water till the reaction was neutral. Crystallisation from acetic acid afforded yellowish crystals which had a diffuse melting point at about 230°C, resolidified and melted again at 320–322°C. Ref.<sup>2,3</sup> reports m.p. 220–230°C. According to thin-layer chromatography (chloroform with 2% of 2-propanol) the product contained the dihydropyridone *I* ( $R_F$  0.35) and the pyridone *III* ( $R_F$  0.30). Quantitative analysis of both components was performed by  $^1\text{H-NMR}$  spectroscopy (Table III). The crude product was filtered and the filtrate extracted with ether, the organic layer washed with a sodium hydrogen carbonate solution, dried over magnesium sulphate and taken down. The residue contained 1,3-diphenyl-1-propanone ( $R_F$  0.64), as proved by thin-layer chromatography (benzene) with an authentic sample.

## Reaction of Benzylideneacetophenone with Ethyl Cyanoacetate

The reaction of the title compound with ammonium acetate in benzene was performed according to ref.<sup>9</sup> and afforded yellowish crystals, m.p. 220–222°C (reported<sup>9</sup> m.p. 222–224°), which were a mixture of *I* and *III*, as shown by thin-layer chromatography and  $^1\text{H-NMR}$  spectra (Table III).

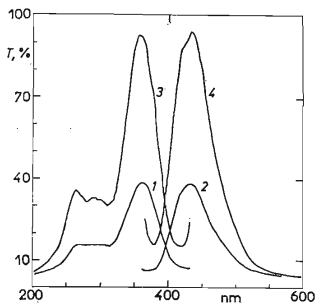


FIG. 1

Electronic Spectrum of 3-Cyano-4,6-diphenyl-2-pyridone (*III*) in Methanol

1 Absorption curve for  $c 2 \cdot 10^{-6}\text{M}$ ; 2 emission curve for  $c 2 \cdot 10^{-6}\text{M}$ ; 3 absorption curve for  $c 10^{-5}\text{M}$ ; 4 emission curve for  $c 10^{-5}\text{M}$ .

3-Cyano-4,6-diphenyl-3,4-dihydro-2-pyridone (*I*)

A mixture (500 mg) of compounds *I* and *III* (prepared according to ref.<sup>4</sup>) was dissolved in chloroform (50 ml) and this solution was chromatographed on loose layer of Silpearl UV 254 (Kavalier, Votice, Czechoslovakia; plates 25 × 15 × 3 mm, zonal application of 10 ml solution per plate, ascending arrangement, chloroform-ethyl acetate (85 : 15), zones detected by UV lamp). Extraction of the pertinent parts of adsorbent with methanol afforded 300 mg of *I*, m.p. 220–221°C.

3-Cyano-4,6-diphenyl-3-methyl-3,4-dihydro-2-pyridone (*V*)

Sodium hydride (672 mg) was added under nitrogen at 5°C to a stirred solution of a mixture of *I* and *III* (5.5 g) (prepared according to ref.<sup>4</sup>) in dimethylformamide (100 ml). The reaction mixture was stirred at 40°C for 1 h, cooled to 10°C and methyl iodide (4 g) was added. After warming to 40°C for one hour further methyl iodide (2 g) was added. The mixture was kept for 4 h at this temperature, poured into ice-cold water (100 ml) and the precipitate (5.2 g) was filtered, washed with water and dried over phosphorus pentoxide. According to thin-layer chromatography (chloroform with 2% dimethylformamide), the product contained the 3-methyl derivative *V* ( $R_F$  0.58) and the pyridone *III* ( $R_F$  0.30) as the main components and melted at 242–244°C (acetone-water 1 : 1). A sample (500 mg) was chromatographed on an alumina column (50 g, activity III, chloroform) and from 471 mg of the fractionated material the compound *V* (170 mg) was obtained; m.p. 244–245°C. For  $C_{19}H_{16}N_2O$  (288.3) calculated: 79.14% C, 5.59% H, 9.71% N; found: 79.26% C, 5.86% H, 9.63% N.

3-Cyano-4,6-diphenyl-1,3-dimethyl-3,4-dihydro-2-pyridone (*VI*)

A mixture of compounds *I* and *III* (5.48 g), prepared according to ref.<sup>4</sup>, sodium hydride (1 g) and methyl iodide (7.92 g) in dimethylformamide (100 ml) were stirred in a nitrogen atmosphere at 40°C for 8 h. The reaction mixture was diluted with water, the separated product was extracted with benzene, the extract dried over magnesium sulphate and taken down *in vacuo*. Crystallisation of the residue at very low temperature from ethanol afforded 2 g of the compound *VI*, m.p. 143–145°C. Thin-layer chromatography (chloroform) of this product showed a single spot,  $R_F$  0.31. For  $C_{20}H_{18}N_2O$  (302.4) calculated: 79.44% C, 6.00% H, 9.26% N; found: 79.41% C, 6.08% H, 9.19% N.

3-Cyano-4,6-diphenyl-1,3-diethyl-3,4-dihydro-2-pyridone (*VII*)

The reaction of the mixture of *I* and *III* (5.48 g) with sodium hydride (0.96 g) and ethyl iodide (6.3 g), as well as the isolation of the crude product, was carried out similarly as described in the preceding experiment. The oily residue set to crystals only after several weeks of storage at room temperature, affording thus 1.2 g of the compound *VII* which upon crystallisation from ethanol melted at 136–138°C. Thin-layer chromatography (chloroform) exhibited only one spot,  $R_F$  0.38. For  $C_{22}H_{22}N_2O$  (330.4) calculated: 79.97% C, 6.71% H, 8.48% N; found: 80.27% C, 6.75% H, 8.14% N.

3-Cyano-2-methoxy-4,6-diphenylpyridine (*VIII*)

The reaction of the compound *III* (1 g) with sodium hydride (200 mg) and methyl iodide (1.9 g) in dimethylformamide (50 ml) was performed analogously to the abovementioned preparations (40°C, 6 h). After dilution with water the separated product was filtered and crystallised from ethanol, yielding 500 mg of the compound *VIII*, m.p. 94–96°C; reported m.p.<sup>12</sup>: 96–97°C;



thin layer chromatography (chloroform) showed a single spot,  $R_F$  0.74.  $^1\text{H-NMR}$  spectrum,  $\delta$  (ppm): 4.16 s ( $\text{OCH}_3$ ), 7.75 s (HC) and 7.2–8.3 m ( $\text{C}_6\text{H}_5$ ). For  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$  (286.3) calculated: 79.70% C, 4.93% H, 9.78% N; found: 79.53% C, 5.30% H, 10.09% N.

#### Dehydrogenation of the Dihydro Derivative *I* (see equation (A))

A mixture of the compound *I* (1 g), benzylideneacetophenone (2 g), sodium hydroxide (50 mg) and ethanol (50 ml) was refluxed for 8 h. After cooling the separated product was filtered and crystallised from ethanol, yielding 750 mg of the pyridone *III*, m.p. 322–324°C.

#### Oxidation of the Dihydro Derivative *I*

A mixture of the compounds *I* and *III* (2 g) in acetic acid (50 ml) was oxidized with chromium trioxide (1.5 g) according to ref.<sup>8</sup>. The product was crystallised twice from acetic acid and afforded 500 mg of the chromatographically pure pyridone *III*. Analogously, the oxidation of a mixture of *I* and *III* (2.5 g) with nitrous acid<sup>2</sup> gave 1 g of the pyridone *III*.

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