

## STABLE 2H-PYRAN DERIVATIVES ACCESSIBLE BY CYCLOCONDENSATION OF *p*-SUBSTITUTED BENZOYLACETONITRILES

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The 2H-pyrans *Ila-f* can be prepared by thermal cyclocondensation of the ketonitriles *Ia-f*. The alternative structure *III* of the compounds obtained has been excluded unambiguously on the basis of spectral data. The compounds *VII* to *XI* have been isolated as byproducts of the said cyclocondensation of the compound *Ia* in acetic acid with catalysis of ammonium acetate. Probable course of the reaction investigated is discussed.

The known derivatives of the yet not described 2H-pyran do not show high stability due to easy electrocyclic ring opening of the heterocycle with formation of the corresponding dienones<sup>1-4</sup>, so that only some 2,2-disubstituted compounds<sup>3-12</sup> can usually be isolated. In a previous communication<sup>10</sup> it was shown that a deeply yellow considerably stable product can be isolated from thermal condensation reaction of benzoylacetonitrile (*Ia*), the suggested structure<sup>13</sup> of the former being 3,5-dicyano-2-cyanomethyl-2,4,6-triphenyl-2H-pyran (*Ila*). The mentioned stability (m.p. 305–306°C without decomposition), which is apparently surprising, is connected undoubtedly with the presence of the 3,5-cyano groups whose stabilizing effect on similar heterocyclic systems was observed with analogous 1,2-dihydropyridines<sup>14-17</sup> and 4H-pyrans<sup>18-20</sup>. As the said preparation<sup>13</sup> of the compound *Ia* seemed to be the only passable method of ring closure of 2H-pyran system from three molecules of 3-ketonitrile, we were interested in the extent to which it can be applied also for further *p*-substituted starting substances *Ib-e*. Furthermore, we considered useful to determine which further isolable products of transformations of the compound *Ia* are present in the reaction mixture. This communication presents the results of the experimental studies of the mentioned problems.

The formerly used preparation method of the compound *Ila* from a melt of the ketonitrile *Ia* has now been modified by using xylene and acetic acid as solvents and ammonium acetate as catalyst and with continuous removal of the water formed in the course of the reaction by azeotropic distillation. In this way it was possible to increase the yield of the yellow product from the compound *Ia* from 22% to 46% (Table I). The ketonitriles *Ib-e* under the same reaction conditions gave analogous

TABLE I  
Properties of the Newly Prepared Cyclocondensation Products

Compound (yield, %)	M.p., °C (solvent)	Formula (mol. mass)	Calculated/Found		$\delta$ , ppm $\delta(X)$ $\delta(CH_2)$	$\delta(C_5D_5N, 70^\circ C)$ $\delta(H\text{-arom.})$	$\nu_{max}$ , $cm^{-1}$ $\nu(C=N)^d$	$\lambda$ , nm $\lambda_{max}$	$\log \epsilon$
			% C	% H					
<i>Iib</i> (53) <sup>b</sup>	264—266 (toluene)	C <sub>30</sub> H <sub>23</sub> N <sub>3</sub> O (441.5)	81.61	5.25	9.52	2.26s	2.238	255	4.41
<i>Iic</i> (26)	283—284 (DMSO, DMF)	C <sub>30</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub> (489.5)	81.88	5.66	9.16	2.30s	2.211	364	4.48
			73.60	4.74	8.58	4.01s <sup>c</sup>	2.231	318	4.45
			73.87	4.83	8.71	4.03s 4.04s	2.200	400	4.41
<i>Iid</i> (45)	356—358 (DMSO, DMF)	C <sub>27</sub> H <sub>14</sub> Cl <sub>3</sub> N <sub>3</sub> O (502.8)	64.50	2.81	8.36 <sup>d</sup>	— <sup>e</sup>	2.220	291	4.77
			64.75	2.89	8.58 <sup>d</sup>	—	2.200	370	4.44
<i>Iie</i> (90)	257—259 (toluene)	C <sub>45</sub> H <sub>29</sub> N <sub>3</sub> O (627.4)	86.10	4.66	6.69	—	2.225	322	4.68
			86.05	4.93	6.52	—	2.205	377	4.51
<i>Iif</i> (19) <sup>g</sup>	325—327 (toluene)	C <sub>27</sub> H <sub>14</sub> F <sub>3</sub> N <sub>3</sub> O (453.4)	71.52	3.11	9.27	108.86s <sup>i</sup>	2.238	290	4.46
			h	h	8.92	108.71s 109.92s	2.215	365	4.44
<i>VIII</i> (1.8) <sup>b</sup>	(ethanol)	C <sub>26</sub> H <sub>17</sub> N <sub>3</sub> (371.4)	84.08	4.64	11.30	— <sup>e</sup>	2.250	282	4.60
<i>X</i> (3.1) <sup>b</sup>	317—318 (benzene)	C <sub>36</sub> H <sub>22</sub> N <sub>4</sub> O (526.6)	84.08	4.61	11.20	2.49s <sup>j</sup>	2.232	275	4.52
			82.11	4.21	10.64	—	2.205	314	4.35
<i>XI</i> (3.7) <sup>b</sup>	304—305 (methanol)	C <sub>36</sub> H <sub>22</sub> N <sub>4</sub> O (526.6)	82.09	4.34	10.86	—	2.230 <sup>l</sup>	442	4.53
			82.11	4.21	10.64	3.60s	2.230 <sup>l</sup>	465	4.45
			81.74	4.31	10.44	6.40—8.50m <sup>k</sup>	2.230 <sup>l</sup>	276	4.80
								385	4.35
								403	4.37

<sup>a</sup> The compounds *Iib*—*f* were measured by the KBr technique, the compounds *VIII*, *X* and *XI* were measured in chloroform; <sup>b</sup> under identical conditions we obtained 46% yield of the compound *Iia*, m.p. 305—306°C (ref. 13 gives m.p. 305—306°C); <sup>c</sup> measured in CF<sub>3</sub>CO<sub>2</sub>H at 37°C; <sup>d</sup> calculated: 21.15% Cl, found: 21.17% Cl; <sup>e</sup> in DMSO at 140°C; <sup>f</sup> the signal is overlapped by absorption of the solvent; <sup>g</sup> different way of preparation (see Experimental); <sup>h</sup> not analyzed; but calculated: 12.57% F, found: 13.10% F; <sup>i</sup> the <sup>19</sup>F chemical shifts related to CDCl<sub>3</sub> after the proton decoupling; <sup>j</sup> measured in CDCl<sub>3</sub> at 37°C; <sup>k</sup> in CDCl<sub>3</sub> at 35°C it was found: 3.50 s, 1.5 s (very broad), 6.28—8.24 m and 9.06 s (broad); <sup>l</sup> besides that we identified also the bands at 3 380 cm<sup>-1</sup> (NH) and 1 684 cm<sup>-1</sup> (C=O).

products of general formula  $C_{27}H_{14}N_3OX_3$  with similar UV, IR and  $^1H$ -NMR spectral characteristics, their yields varying within 26% to 90%. Hence it can be concluded that the investigated cyclocondensation reaction of ketonitriles type *I* has a broader scope.

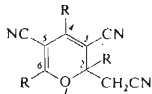
Out of the two pyran structures *Ila* and *IIla* the former was considered correct<sup>13</sup> on the basis of the finding that the compound does not react with ammonia to give the corresponding 1-aza analogue, as it is the case with 4*H*-pyrans<sup>21-23</sup>. We have now tried to replace this indirect argument in favour of the 2*H*-pyran structure by direct evidence on the basis of NMR study of the *p*-substituted derivatives *Ib,c*. If the general structure *II* of the cyclocondensation products is correct, then each of the molecules *Ib,c* must contain three non-equivalent methyl groups, whereas the 4*H*-isomers *IIIb,c* contain but two. The  $^1H$ -NMR spectra measured at 100 MHz (under normal conditions) could reveal only two singlets of methyl protons at 2.26 and 2.30 $\delta$  in the product obtained from the 4-methyl derivative *Ib*. The latter maximum and the substantially more intensive absorption is, however, split into two components with a very small separation of about 1 Hz after decoupling of the protons at *ortho* positions of the aromatic nuclei. On the contrary, in the 100 MHz spectrum of the product from the 4-methoxy compound *Ic* it was possible to identify three close singlets of methyl protons at 4.01, 4.03 and 4.04 $\delta$ , the decoupling experiments being unnecessary. These results support the 2*H*-pyran structures of the compounds investigated (*Ib,c*), nevertheless, their value is considerably lowered by the too small differences in the chemical shifts of the partially overlapped signals. Furthermore, the  $^{13}C$  signals of the mentioned methyl groups could not be measured due to extremely low solubility of the investigated pyrans in available solvents. Therefore, we decided to differentiate between the two alternative structures *II* and *III* by using  $^{19}F$ -NMR spectra (an analogous approach was applied independently in ref.<sup>24</sup>, too).

Therefore, we prepared *p*-fluorobenzoylacetonitrile (*If*) by condensation of ethyl *p*-fluorobenzoate (*IV*) with acetonitrile catalyzed by sodium hydride. Application of the procedure with sodium ethoxide<sup>25</sup> fails in this case, because formation of the ketonitrile *If* is suppressed by predominant nucleophilic substitution of fluorine atom in the ester *IV* giving ethyl *p*-ethoxybenzoate (*V*). Thermal decomposition of the compound *If* gave a 19% yield of the expected yellow cyclocondensation product  $C_{27}H_{14}N_3OF_3$  which unambiguously showed in its proton-decoupled  $^{19}F$ -NMR spectrum three singlets of identical integral intensities at 108.7, 108.9, and 109.9 $\delta$ . This finding can be considered unambiguous evidence of the 2*H*-pyran structure *IIIf* and exclusion of the alternative *IIIIf*. On the basis of similarity of the characteristic  $^1H$ -NMR, IR and UV spectral data in Table I it is then possible to exclude, *per analogiam* also in the other cases, the structures *IIIa,d,e* and to consider only the formulas *IIa,d,e* to be correct.

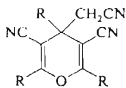
Chromatography of the reaction mixture obtained by reaction of the ketonitrile *Ia* in the presence of ammonium acetate revealed that the mother liquors after separation

of the little soluble 2*H*-pyran *IIa* contained at least five other compounds in smaller amounts. Out of them it was possible to isolate four individual compounds by means of adsorption preparative chromatography: the known<sup>26</sup> 6-amino-2,4-diphenyl-3-cyanopyridine (*VII*), a colourless crystalline solid C<sub>26</sub>H<sub>17</sub>N<sub>3</sub> melting at 217–219°C and two yellow isomers C<sub>36</sub>H<sub>22</sub>N<sub>4</sub>O melting at 304–305°C and 317–318°C, respectively. The colourless substance was ascribed the structure of 5-cyano-2,4,6-triphenyl-3*H*-pyrrolo[4,5-*b*]pyridine (*VIII*) on the basis of <sup>1</sup>H-NMR spectrum showing one

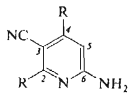
RCOCH<sub>2</sub>CN



*IIa-f*



*IIIa-f*



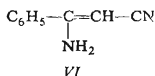
*VII* (R = C<sub>6</sub>H<sub>5</sub>)

- Ia*, R = C<sub>6</sub>H<sub>5</sub>
- Ib*, R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>
- Ic*, R = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>5</sub>
- Id*, R = *p*-ClC<sub>6</sub>H<sub>4</sub>
- Ie*, R = *p*-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>
- If*, R = *p*-FC<sub>6</sub>H<sub>4</sub>

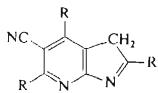
*p*-XC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>

*IV*, X = F

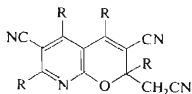
*V*, X = C<sub>2</sub>H<sub>5</sub>O



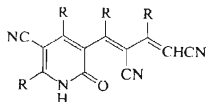
*VI*



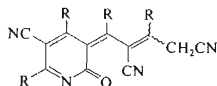
*VIII* (R = C<sub>6</sub>H<sub>5</sub>)



*X* (R = C<sub>6</sub>H<sub>5</sub>)



*XI* (R = C<sub>6</sub>H<sub>5</sub>)



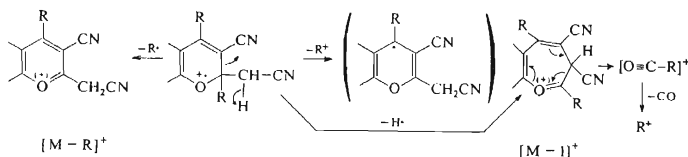
*XII*

CH<sub>2</sub> group (a singlet at 2.94δ) and three C<sub>6</sub>H<sub>5</sub> groups (multiplets within 7.3 to 8.2δ) and on the basis of IR spectrum showing an aromatically bound CN group (2250 cm<sup>-1</sup>). Comparison of <sup>13</sup>C-NMR spectra of the both compounds *VII* and *VIII* (Table II) can be considered a further argument in favour of the said structural conclusions. Out of the yellow isomers the higher-melting form exhibits an <sup>1</sup>H-NMR spectrum with four C<sub>6</sub>H<sub>5</sub> groups (a multiplet at 6.9 to 8.4δ) and a CH<sub>2</sub>CN group (a singlet at 2.21δ) and an IR spectrum with two types of cyano groups (2232 and 2205 cm<sup>-1</sup>) with the absence of C=O, NH and OH bonds. On the basis of these findings the higher-melting isomer is ascribed the constitution of 3,6-dicyano-7-cyano-methyl-2,4,5,7-tetraphenyl-2*H*-pyrano[5,6-*b*]pyridine (*X*). On the contrary, the molecule of the lower-melting isomer contains, according to its IR spectrum, con-

jugated  $C\equiv N$  and  $C=O$  groups ( $2230$  and  $1684\text{ cm}^{-1}$ ) and an  $NH$  bond ( $3380\text{ cm}^{-1}$ ) and, according to its  $^1H$ -NMR spectrum, four  $C_6H_5$  groups (multiplets at  $6.3$  to  $8.2\delta$ ), a grouping  $=CH-CN$  (singlet at  $3.5\delta$ ), and an  $NH$  group (a broadened singlet at  $1.5$  and another one at  $10\delta$  in deuteriochloroform solutions\*).

These findings allow to formulate the constitution of this isomer as  $5-(1',3'$ -butadienyl)- $2,4,1',3'$ -tetraphenyl- $2',3',4'$ -tricyano- $6$ -pyridone ( $XI$ ).

The suggested constitutions of the investigated compounds  $IIb-f$  and  $VII-XI$  agree with fragmentation of the respective molecules by electron impact (Schemes 1



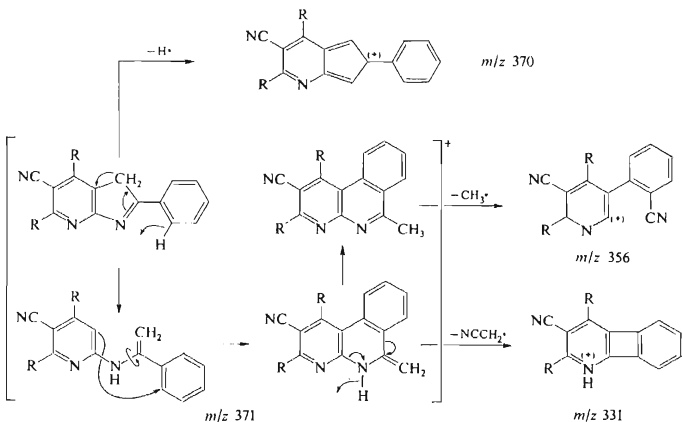
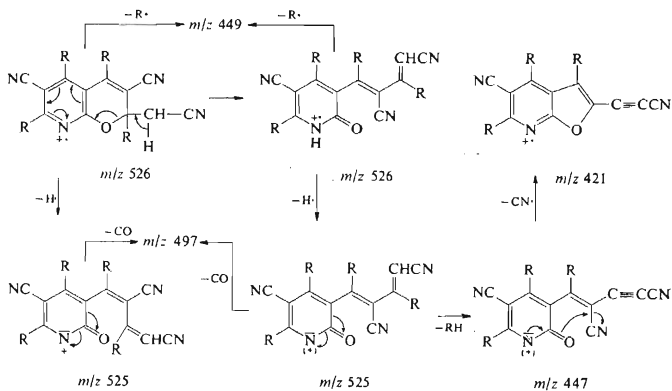
SCHEME 1

and 2). The existence of  $2H$ -pyran cycle in the compounds  $IIa-f$  and  $X$  makes itself felt by formation of the ionic species  $[M-1]^+$ ,  $[M-R]^+$ ,  $[RCO]^+$  and  $[R]^+$  the formation of which is proposed in Scheme 1. The fact that the ionic species  $m/z$  105 corresponding to the particles  $[C_6H_5CO]^+$  is also generated by fragmentation of molecular ion of the bicyclic derivative  $X$  necessitates to consider its parent ion  $[M-1]^+$  to be a seven-membered heterocycle in accordance with findings in similar cases<sup>27</sup> but in contrast to the formerly presumed<sup>13</sup> bicyclic structure for interpretation purposes of spectrum of compound  $IIa$ . Besides that the spectra of the individual derivatives  $IIb-f$  only differ in occurrence and number of ionic species in the region of low  $m/z$  values due to various fragmentation of the particles  $[R]^+$  where  $R = X-C_6H_4$ .

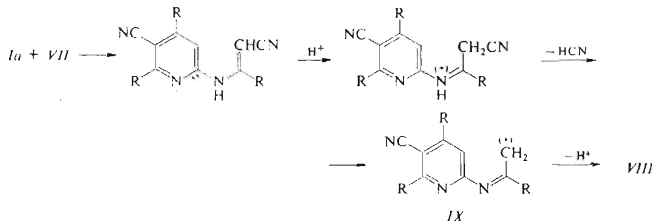
The Scheme 2 interpretes the characteristic differences in mass spectra of the both isomers  $X$  and  $XI$ . Besides the identical ionic species  $m/e$  525, 497, 449, 77, 51 and 50 the isomer  $XI$  generates further ionic species out of which the structural genesis of the fragments  $m/z$  447 and 421 seems to be obvious. The fact that the compound  $XI$  is not a  $2H$ -pyran derivative agrees with the absence of the ionic species  $[C_6H_5CO]^+$ , i.e.  $m/z$  105 in its spectrum. Fragmentation of the molecular ion of compound  $VIII$  shows the most frequent ionic species at  $m/z$  370, 356 and 331. Their formation is explained in Scheme 3.

\* This absorption depends strongly on solvent and temperature. It is probably connected with hydroxypyridine-pyridone tautomerism of the investigated compound.

The presence of smaller amounts of the compounds VII and VIII in the reaction mixture can be explained by participation of ammonium acetate in the reaction



course. In the reaction  $Ia + CH_3CO_2NH_4 \rightarrow VI + CH_3CO_2H$  the formed enamino-nitrile *VI* undergoes the described condensation<sup>28</sup> to give 6-amino-2,4-diphenyl-3-cyanopyridine (*VII*) according to the equation  $2 VI + CH_3CO_2H \rightarrow VII + CH_3CO_2NH_4$ . Formation of the pyrrolo-pyridine derivative *VIII* is explained in Scheme 4. The first step consists in condensation of the amino derivative *VII*



SCHEME 4 (R = C<sub>6</sub>H<sub>5</sub>)

TABLE II

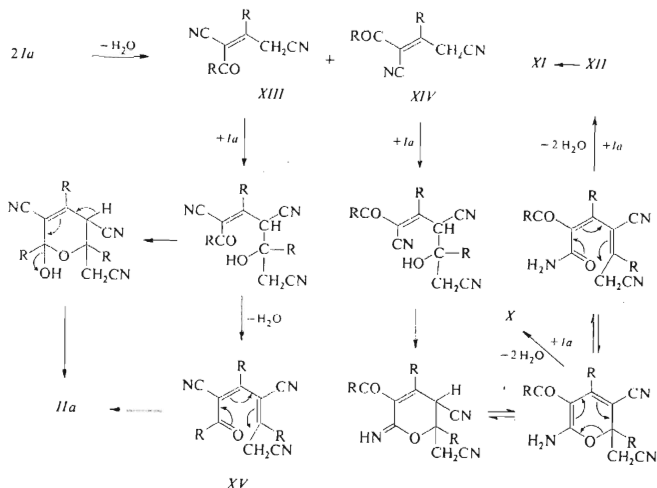
<sup>13</sup>C-NMR Chemical Shifts of the Compounds *VII* and *VIII*

The data in ppm with respect to tetramethylsilane, saturated solutions in hexadeuteriodimethyl sulphoxide.

Signal No	Compound <i>VII</i>		Compound <i>VIII</i> <sup>a</sup>	
	δ	assignment	δ	assignment
1	163.23	NC(6)N	162.79	C(2)N
2	160.91	C(2)N	159.69	NC(8)N
3	153.82	C(4)	141.05	C(6)N
4	138.70	<i>ipso</i> -C <sup>b</sup>	138.44	<i>ipso</i> -C <sup>b</sup>
5	137.51	<i>ispo</i> -C <sup>c</sup>	136.65	<i>para</i> -C <sup>b</sup>
6	129.70	<i>para</i> -C <sup>b</sup>	134.26	C(4)
7	129.52	<i>para</i> -C <sup>c</sup>	131.64	<i>ipso</i> -C <sup>c</sup>
8	129.08	<i>meta</i> -C <sup>b</sup>	131.40	<i>para</i> -C <sup>c,d</sup>
9	128.92	<i>meta</i> -C <sup>c</sup>	129.74	<i>meta</i> -C <sup>b,c,d</sup>
10	128.54	<i>ortho</i> -C <sup>b</sup>	129.41	<i>ipso</i> -C <sup>d</sup>
11	128.35	<i>ortho</i> -C <sup>c</sup>	128.92	<i>ortho</i> -C <sup>b,c,d</sup>
12	119.33	C≡N	126.50	C(9)
13	106.62	C(3)	116.31	C≡N
14	92.74	C(5)	106.56	C(5)

<sup>a</sup> Besides the signals given the spectrum contains another one for the group CH<sub>2</sub> (position 3) at -18.49 ppm; <sup>b</sup> for 2-phenyl group; <sup>c</sup> for 4-phenyl group; <sup>d</sup> for 6-phenyl group.

with the ketonitrile *Ia* followed by the acid-catalyzed generation of the carbocation *IX* which attacks the pyridine nucleus to give the product *VIII*.



SCHEME 5 (R = C<sub>6</sub>H<sub>5</sub>)

Scheme 5 explains the formation of the byproducts *X* and *XI* besides the main product *IIa*. Obviously it is necessary to presume a relative great number of non-isolated intermediates which are rapidly transformed into the mentioned isolated products under the reaction conditions. It is useful to ascribe the role of key intermediates to the stereoisomeric dicyanides *XIII* and *XIV*, the former of which leads generally to the 2*H*-pyran derivative *IIa*, whereas the latter gives pyrido-2*H*-pyran derivative *X* and pyridone *XI*. Most likely the tautomer *XI* having a more extended pi-electron structure is considerably preferred energetically with respect to the tautomer *XII*, and consequently it is possible only to isolate the isomerization product (*XII* → *XI*) instead of the equilibrium mixture. The attempts to prove chromatographically (TLC) the isomerization  $XI \rightleftharpoons X$  above the melting point of the both isomers *X* and *XI* were negative.

#### EXPERIMENTAL

The temperature data are not corrected. The melting points were determined with a Boetius apparatus. The spectral characteristics were measured with a Perkin-Elmer 325 (IR), Carl Zeiss



Jena Specord UV VIS, Varian XL—100 ( $^1\text{H-NMR}$ ,  $^{19}\text{F-NMR}$ , and  $^{13}\text{C-NMR}$ ), LKB 9000, AEI MS 9 and Varian MAT 311 A (MS, 70 eV) apparatus.

**Benzoylacetonitriles Ia—c.** The compounds *Ia—d* were prepared by reaction of the corresponding benzoates with acetonitrile<sup>25</sup> in the presence of sodium ethoxide. The found melting points: 80—81°C (*Ia*), 101—102°C (*Ib*), 127—129°C (*Ic*), and 124—129°C (*Id*); the respective literature data<sup>25</sup>: m.p. 80—81°C, 94—99°C, 126—129°C, and 125—129°C. The 4-phenyl derivative *Ie* was prepared similarly with the yield 43% colourless crystals m.p. 112—113°C (from benzene). For  $\text{C}_{15}\text{H}_{11}\text{NO}$  (221.2) calculated: 81.43% C, 5.11% H, 6.20% N; found: 81.50% C, 5.11% H, 6.20% N. UV spectrum (ethanol):  $\lambda_{\text{max}}$  290 nm ( $\log \epsilon$  4.38); IR spectrum ( $\text{CHCl}_3$ ):  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 2260 ( $\text{C}\equiv\text{N}$ ) and 1697 ( $\text{C}=\text{O}$ );  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ )  $\delta$ , ppm: 4.08 s ( $\text{CH}_2\text{CN}$ ) and 7.29—8.09 m ( $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4$ ). Mass spectrum,  $m/z$  (rel. intensity, %): 222 (6.0); 221 (38.8), 182 (14.9) 181 (100); 154 (31.3), 153 (44.7); 152 (14.1); 91 (10.4), 77 (26.8). When the condensation<sup>25</sup> was carried out with ethyl 4-fluorobenzoate (*IV*) it gave exclusively ethyl 4-ethoxybenzoate (*V*) in the yield 75%, b.p. 138—140°C/1.56 kPa; ref.<sup>29</sup> gives bp. 142°C/1.46 kPa. For  $\text{C}_{11}\text{H}_{14}\text{O}_3$  (194.2) calculated: 68.02% C, 7.26% H; found: 68.20% C, 7.43% H. IR spectrum (capillary layer),  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1712 ( $\text{C}=\text{O}$ ) and 1272 ( $\text{C}-\text{O}$ );  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ )  $\delta$ , ppm: 1.38 t ( $\text{CH}_3$ ), 1.41 t ( $\text{CH}_3$ ), 1.41 t ( $\text{CH}_3$ ), 4.03 q ( $\text{CH}_2\text{O}$ ), 4.33 q ( $\text{CH}_2\text{O}$ ), 6.82—8.01  $\text{A}_2\text{B}_2$  ( $-\text{C}_6\text{H}_4-$ ).

**4-Fluorobenzoylacetonitrile (If).** Ethyl ester *IV* (50 g) was heated with 24 ml acetonitrile and 6.9 g sodium hydride in 800 ml benzene to gentle boiling with intensive stirring for 14 h. Then the reaction mixture was cooled, decomposed by addition of 120 ml ethanol, 400 ml water and 400 ml ether. The aqueous layer was separated, acidified with diluted sulphuric acid (1 : 1) to pH 3 and extracted with 5  $\times$  500 ml ether. The combined ethereal portions were extracted with 300 ml saturated solution of sodium hydrogen carbonate, again with 300 ml water, and finally dried over magnesium sulphate. Evaporation of the solvent gave 15.3 g (31%) colourless needles of the compound *If* which were recrystallized from *n*-heptane (charcoal); m.p. 85—86°C. For  $\text{C}_9\text{H}_6\text{FNO}$  (163.1) calculated: 66.26% C, 3.71% H, 8.59% N, 11.64% F; found: 66.47% C, 3.93% H, 8.53% N, 11.56% F. UV spectrum (ethanol),  $\lambda_{\text{max}}$  247 nm ( $\log \epsilon$  4.09), IR spectrum ( $\text{CHCl}_3$ ),  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 2258 ( $\text{C}\equiv\text{N}$ ), 1701 ( $\text{C}=\text{O}$ );  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ )  $\delta$ , ppm: 4.11 s ( $\text{CH}_2\text{CN}$ ), 7.03—8.09 m ( $\text{C}_6\text{H}_4\text{F}$ ). Mass spectrum,  $m/z$  (rel. intensity, %): 163 (6.6); 124 (9.0); 123 (100); 96 (4.9); 95 (57.4); 75 (23), 74 (6.6).

**3,5-Dicyano-3-cyanomethyl-2,4,6-tri(4-X-phenyl)-2H-pyrans IIa—e.** 1 Mol of the respective ketonitrile *Ia—e*, 0.1 mol ammonium acetate, 0.4 mol acetic acid and 670 ml technical xylene were heated to boiling with continuous removal of the reaction water in azeotropic distillation head. After the formation of reaction water was finished (about 4 to 8 h), 200 ml xylene was distilled off from the reaction mixture and the distillation residue was cooled. The separated crystals of the respective pyran derivatives *IIa—e* were collected by suction and extracted with 3  $\times$  2 l boiling ethanol. The raw product thus obtained was crystallized from the corresponding solvent (charcoal or alumina); the obtained yields, melting points, analytical and spectral data are summarized in Table I.

**3,5-Dicyano-2-cyanomethyl-2,4,6-tri(4-fluorophenyl)-2H-pyran (IIIf).** The ketonitrile *If* (1 g) was melted and further heated at 190 to 200°C for 20 min. After cooling the solidified reaction mixture was crushed and digested with 3  $\times$  50 ml boiling ethanol, and the insoluble residue was recrystallized from toluene using alumina as adsorbent to remove the deeply coloured impurities. Yield 176 mg (19%) pyrene derivative *IIIf*, m.p. 325—327°C; its further properties are given in Table I.

**Isolation of products of concentration reactions of compound Ia.** The ketonitrile *Ia* (218 g), 11.6 g ammonium acetate, 60 ml acetic acid and 1 l xylene were heated to boiling for 12 h with conti-

nuous removal of the reaction water in azeotropic distillation head. The pyran derivative *Ia* separated on cooling (82 g, 46%) was collected by suction, and the mother liquor was submitted to further azeotropic condensation reaction for 9 h. After removal of a resinous portion the solvent was vacuum-distilled, and the distillation residue (60 g) was submitted to column chromatography: 30 g distillation residue and 2 kg alumina activity II. The following eluents were successively used: 2·7 l mixture chloroform-tetrachloromethane (1 : 1), 1·8 l the same mixture 2 : 1, 4·5 l the same mixture 3 : 1, 2 l chloroform, 2 l chloroform with 1% ethanol, 2 l the same mixture with 2%, 5 l with 4%, 3 l with 12% ethanol, 2 l ethanol (total 96 fractions of about 250 to 300 ml volume). Composition of the individual fractions was checked by TLC (alumina, detection in UV light and in iodine vapours), which revealed the presence of total five low-molecular compounds, out of which four could be obtained in pure state in the eluates. The fractions 4 to 7 gave 1·7 g colourless crystals of the compound *VIII* which was repeatedly crystallized from ethanol; m.p. 204–206°C. The fractions 28 to 30 contained mixture of the compounds *X* and *VII* (4·8 g), and its fraction crystallization from ethanol and benzene (successively) gave 3·1 g yellow crystals of the pyrano-pyridine derivative *X*, m.p. 317–318°C, and colourless crystals of amino-pyridine *VII*, m.p. 217–219°C (ref.<sup>26</sup> gives m.p. 214–215°C for the hemihydrate), whose spectral characteristics were identical with those of the substance prepared by independent synthesis. IR spectrum ( $\text{CHCl}_3$ )  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 3530, 3435 ( $\text{NH}_2$ ), 2230 ( $\text{C}\equiv\text{N}$ ).  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 5·04 s ( $\text{NH}_2$ ), 6·46 s (=CH), 7·30–7·90 m ( $\text{C}_6\text{H}_5$ ). The fractions 57 to 72 (3·7 g) contained the yellow pyridone derivative *XI* which melted at 304–305°C after repeated crystallization from methanol. Analytical and spectral data of the compounds *VIII*, *X* and *XI* are given in Tables I and II.

6-Amino-3-cyano-2,4-diphenylpyridine (*VII*). Mixture of 5 g compound *Ia* and 8 g phosphoryl trichloride was heated at 60–70°C for 2 h, and poured onto 100 ml ice and water. The separated solid was collected by suction and recrystallized from ethanol to give 2·3 g 6-chloro-3-cyano-2,4-diphenylpyridine, m.p. 179–181°C (ref.<sup>26</sup> gives m.p. 178–180°C). This chloro derivative was heated with 25 ml ethanolic ammonia (3·5 g  $\text{NH}_3$ ) at 160–170°C in a pressure ampoule 5 h. The solvents were evaporated and the residue was crystallized from ethanol to give 1·75 g compound *VII*, m.p. 217–219°C (ref.<sup>26</sup> gives m.p. 214–215°C for the hemihydrate). For  $\text{C}_{18}\text{H}_{13}\text{N}_3$  (271·0) calculated: 79·68% C, 4·83% H, 15·49% N; found: 79·53% C, 5·01% H, 15·60% N.

*Mass spectra* (ions and relative %). *Iib*: 442 (31·2), 441 (100), 440 (55·1), 350 (15·0), 326 (12·2), 322 (4·1), 200 (8·2), 119 (55·1), 91 (95·9), 65 (30·6), 51 (4·1). *Iic*: 490 (30·5), 489 (100), 488 (22·5), 382 (5·2), 354 (2·7), 135 (26·7), 107 (15·2), 78 (38·4), 77 (11·6). *IId*: 506 (12·6), 505 (35·7), 504 (39·7), 503 (100), 502 (64·3), 501 (100), 500 (39·3), 392 (19·3), 391 (7·9), 390 (28·6), 141 (21·4), 139 (60·7), 113 (21·4), 111 (50·0), 99 (17·9), 97 (25·0), 85 (39·3), 83 (25·0). *Iie*: 629 (32·4), 628 (56·2), 627 (100), 594 (7·2), 470 (3·5), 415 (11·1), 314 (8·2), 296 (6·7), 181 (6·1), 161 (6·1), 155 (2·8). *IIf*: 454 (34·4), 453 (100), 452 (44·4), 359 (6·7), 358 (25·9), 330 (4·8), 329 (6·7), 123 (18·6), 95 (26·5), 69 (5·2), 51 (9·4). *VII*: 272 (21·4), 271 (90·7), 270 (100), 254 (15·2), 253 (25·0), 243 (5·7), 227 (4·3), 226 (4·3), 140 (16·4), 104 (15·8), 77 (26·4), 76 (15·8), 51 (26·4), 50 (12·8). *VIII*: 372 (11·1), 371 (42·5), 370 (37·2), 358 (6·3), 357 (36·8), 356 (100), 332 (7·2), 331 (8·3). *X*: 528 (5·5), 527 (25·5), 526 (65·0), 525 (18·9), 497 (8·3), 449 (24·4), 105 (51·1), 78 (9·8), 77 (100), 51 (50·1), 50 (21·1). *XI*: 527 (25·2), 526 (74·8), 525 (100), 497 (4·6), 495 (3·8), 449 (16·5), 447 (13·2), 421 (5·8), 263 (9·1), 202 (9·0), 77 (76·2), 51 (55·3), 50 (28·4).

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