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Note

Synthesis and Photochemical Behaviour of Substituted 3,4-furandicarboxdianilides

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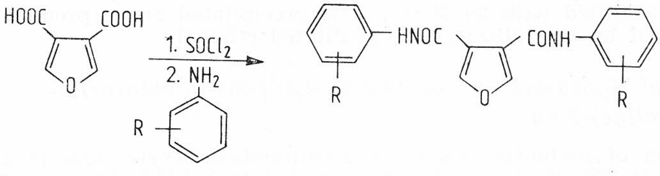
Some substituted 3,4-furandicarboxdianilides were prepared from the corresponding substituted anilines and 3,4-furandicarboxylic acid dichloride. All compounds were exposed to UV irradiation in methanolic solution, but under the conditions applied only *p*-chloro- substituted dianilide dehydrocyclized to the corresponding furo-bis-quinolone.

In our earlier papers we reported on the preparation and properties of some substituted 3-furancarboxanilides[1], as well as on the photochemical cyclization of chloro-substituted 3-furancarboxanilides.[2] Continuing our investigations on the photochemical behaviour of furan compounds we have prepared some aryl-substituted 3,4-furandicarboxylic acid dianilides.

According to the literature data such compounds have not been described so far, only some 2,5-disubstituted 3,4-furandicarboxdianilides were reported.[3,4]

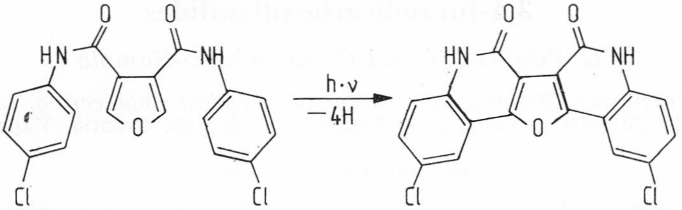
The title compounds (I—VI) have been prepared using 3,4-furandicarboxylic acid as the starting material according to Sheme 1:



Sheme 1

R = *o*-OCH$_3$, *m*-OCH$_3$, *p*-OCH$_3$, *o*-Cl, *m*-Cl, *p*-Cl

All prepared anilides were exposed to UV irradiation. When the irradiation was over, we could isolate the dehydrocyclization product only in the case when *p*-chlorodianilide was the starting compound (Sheme 2). The ^{1}H NMR-spectrum of the obtained furobis-quinolone shows that protons on positions 6 and 6′ are not equivalent because of the nonplanarity of the pentacyclic system. In all other cases there was no dehydrocyclizing, the starting compound was not recovered, only a lot of resins could be isolated. The resinification of *o*-chloro and *m*-chlorodianilides occurred after 7 hours of irradiation with a high pressure mercury arch lamp in quarz and *o*-methoxy-, *m*-methoxy- and *p*-methoxydianilides gave the same results after 24 hours of irradiation under the same reaction conditions. Resinification of these anilides was also observed when 254 nm light was used. We suppose that such results are caused by the electronic and steric effects depending on the kind and position of substituents on the phenyl ring. Structures of all new compounds were confirmed by UV, IR and ^{1}H NMR spectra.



Sheme 2.

EXPERIMENTAL

The melting points are uncorrected. The UV spectra were taken on a Hitachi Perkin-Elmer 124 spectrophotometer using ethanolic solutions. The IR spectra were recorded on a Perkin-Elmer Infracord model 257 spectrophotometer in KBr discs. The ^{1}H NMR spectra were recorded on a 360 Joel J.M.M.-FX—100 FT spectrometer in deuterochloroform or dimethylsulfoxide with TMS as internal reference. Irradiations were performed with a water-cooled quartz immersion equipped with a mercury arc lamp.

General Procedure for the Preparation of 3,4-Furandicarboxdianilides (I—VI)

The title compounds (I—VI) were prepared by dropwise addition of an etheral solution of 3,4-furandicarboxylic acid dichloride[5] in a stirred solution of an equimolar amount of the corresponding amine in pyridine. The reaction mixture was cooled with water keeping the temperature at about 20 °C. After adding the whole amount of dichloride, stirring was continued for half an hour, and then the reaction mixture was acidified with 2n H_2SO_4. The precipitated crude product was filtered off and purified by crystallization from diluted ethanol.

Photochemical Synthesis of Furo[4,3-b; 4,3-']-bis-(6-chloro-1,2-dihydroquinoline)-2-on

A solution of *p*-chlorodianilide of 3,4-furandicarboxylic acid (2 g, 0.005 mole) was dissolved in 700 ml methanol and irradiated with UV light of the high pressure mercury arch lamp T.Q. 150 W original Hanau through the quartz glass during 24 hours at room temperature. Air was bubbled through the solution. The photochemical change was monitored with UV spectroscopy. The solution was then evaporated under reduced pressure, the dark oily residue was chromatographed on the silica gel column with chloroform as eluent. In all fractions it was only possible to detect the dehydrocyclizing product in the yield of 20% melting at about 350 °C with decomp. and with the following spectroscopic data:

UV (λ_{max}): 208 (4,41), 236 (4.34).
IR (cm^{-1}): $_{CO}$1690, $_{NH}$3120.
^{1}H NMR: $H_{4,4}$, 7.41 (2H, d, J = 9.00 Hz), $H_{3,3}$, 7.69 (2H, d, J = 9.0 Hz) H_6 8.51 (1H, d,

TABLE

Substituted 3,4-Furandicarboxdianilides

No	R	Yield %	M. p. °C	UV spectrum λ_{max}/nm (log ε)	IR spectrum		¹H NMR spectrum				Formula (mol. wt.)	Anal. Calcd. found		
					ν CO	N—H/cm^{-1}	H_{fur}	H_{arom}	$H_{N—H}$	H_{OCH_3}		%C	%H	%N
I	o-OCH$_3$	83	110—112	208(4.49871) 272(4.23755)	1655	3340	8.10 (2H, s)	6.84—8.49 (8H, m)	9.84 (2H, s)	3.91 (6H, s)	$C_{20}H_{18}N_2O_5$ (366.38)	65.56 65.68	4.95 5.08	7.65 7.88
II	*m*-OCH$_3$	79	170—172	210(4.51587) 263(4.34830) 295(4.20952)	1660	3310	8.06 (2H, s)	6.65—7.45 (8H, m)	10.14 (2H, s)	3.83 (6H, s)	$C_{20}H_{18}N_2O_5$ (366.38)	65.56 65.63	4.95 4.81	7.65 7.71
III	*p*-OCH$_3$	81	132—133	205(4.50178) 278(4.43411)	1650	3330	8.01 (2H, s)	6.89(4H, d) 7.58(4H, d) $J = 9.08$ Hz	10.00 (2H, s)	3.80 (6H, s)	$C_{20}H_{18}N_2O_5$ (366.38)	65.56 65.39	4.95 5.18	7.65 7.94
IV	*o*-Cl	68	121—122	220(4.53211) 263(4.49725)	1640	3260	8.20 (2H, s)	7.08—8.37 (8H, m)	9.75 (2H, s)		$C_{18}H_{12}Cl_2N_20_3$ (375.22)	57.62 57.39	3.22 3.08	7.47 7.79
V	*m*-Cl	91	178—180	210(4.62014) 250(4.34635) 263(4.34635)	1670	3260	8.05 (2H, s)	6.71—8.02 (8H, m)	9.89 (2H, s)		$C_{18}H_{12}Cl_2N_20_3$ (375.22)	57.62 57.85	3.22 3.30	7.47 7.40
VI	*p*-Cl	85	178—180	218(4.82175) 272(4.12311)	1650	3300	8.10 (2H, s)	7.33(4H, d) 7.63(4H, d) $J = 9.08$ Hz	9.82 (2H, s)		$C_{18}H_{12}Cl_2N_20_3$ (375.22)	57.62 57.33	3.22 3.35	7.47 7.91

$J = 1.8$ Hz), H_6, 8.43 (1H, d, $J = 1.8$ Hz) $H_{2,2}$, 11.5 (2H, s).

Anal. $C_{18}H_8Cl_2N_2O_3$ calc'd.: C 58.24; H 2.17; N 7.55%
found: C 58.35; H 2.30; N 7.28%.

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SAŽETAK

Sinteza i fotokemijske reakcije supstituiranih dianilida 3,4-furandikarboksilne kiseline

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Reakcijom diklorida 3,4-furandikarboksilne kiseline i supstituiranih anilina sintetizirani su neki supstituirani dianilidi 3,4-furandikarboksilne kiseline. Svi dobiveni spojevi izloženi su UV zračenju u metanolnoj otopni, ali u primijenjenim uvjetima samo se *p*-klor-supstituirani dianilid ciklizirao u odgovarajući furo-bis-kinolon.