TABLE I
o-PHTHALIC ACID DIAMIDES

R_3	R_4	Over-all yield, %	Re-crystn solvent[a]	Mp, °C	Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Nitrogen, % Calcd	Nitrogen, % Found
H	H	85	M	257	$C_{14}H_{12}N_2O_2$	70.06	69.88	5.04	4.94	11.67	11.78
H	CH_3	54	E_{abs}	228 dec	$C_{15}H_{14}N_2O_2$	70.87	70.50	5.52	5.92	11.02	11.02
H	C_2H_5	85	E	208	$C_{16}H_{16}N_2O_2$	71.70	71.78	6.02	6.19	10.45	10.10
H	n-C_3H_7	77	E	212	$C_{17}H_{18}N_2O_2$	72.40	72.11	6.43	6.35	9.95	9.95
H	n-C_4H_9	81	E	208	$C_{18}H_{20}N_2O_2$	73.03	73.28	6.81	6.98	9.46	9.44
H	i-C_3H_7	67	E	233	$C_{17}H_{18}N_2O_2$	72.40	72.28	6.43	6.50	9.93	9.68
H	t-C_4H_9	74	E	245	$C_{18}H_{20}N_2O_2$	73.03	73.08	6.81	7.03	9.46	9.20
H	C_6H_{11}	68	E	225	$C_{20}H_{22}N_2O_2$	74.60	74.44	6.89	6.87	8.70	8.87
H	$CH_2C_6H_5$	82	E	203	$C_{21}H_{18}N_2O_2$	76.43	76.56	5.50	5.78	8.49	8.33
H	C_6H_5	67	N	259[b]	$C_{20}H_{16}N_2O_2$	76.01	76.21	5.10	5.11	8.87	9.00
H	o-$CH_3C_6H_4$	78	B	217	$C_{21}H_{18}N_2O_2$	76.43	76.03	5.50	5.32	8.49	8.61
H	m-$CH_3C_6H_4$	81	B	203	$C_{21}H_{18}N_2O_2$	76.43	76.69	5.50	5.70	8.49	8.57
H	p-$CH_3C_6H_4$	73	B	228[c]	$C_{21}H_{18}N_2O_2$	76.43	76.39	5.50	5.38	8.49	8.56
H	o-OHC_6H_4	60	E_{abs}	263	$C_{20}H_{16}N_2O_3$	72.35	72.33	4.86	4.89	8.44	8.67
H	m-OHC_6H_4	74	A_{60}	211	$C_{20}H_{16}N_2O_2$	72.35	72.59	4.86	4.74	8.44	8.53
H	p-OHC_6H_4	75	A_{50}	190	$C_{20}H_{16}N_2O_2$	72.35	72.44	4.86	5.13	8.44	8.53
CH_3	CH_3	39	A_{50}	182	$C_{16}H_{16}N_2O_2$	71.64	72.02	5.97	6.15	10.44	10.05
C_2H_5	C_2H_5	76	A_{50}	124	$C_{20}H_{18}N_2O_2$	73.03	72.95	6.81	6.82	9.46	9.20
$CH_2C_6H_5$	$CH_2C_6H_5$	39	E_{75}	161	$C_{28}H_{24}N_2O_2$	80.07	79.90	5.76	6.03	6.67	6.59
C_5H_{10}		64	A	168.5	$C_{19}H_{20}N_2O_2$	74.90	73.95	6.55	6.59	9.10	9.34

[a] M = MeOH dried following the method of R. Lund and J. Bjerrum [*Ber.*, **64,** 210 (1931)], E_{abs} = EtOH dried by the same method, E = EtOH, N = $C_6H_5NO_2$, B = C_6H_6 dried and distilled over Na, A_{60} = 60% aqueous Me_2CO, A_{50} = 50% aqueous Me_2CO, E_{75} = 75% aqueous EtOH, A = dry Me_2CO. [b] R. D. Reynolds and G. L. Anderson [*J. Org. Chem.*, **28,** 3223 (1963)] report mp 230–231°. [c] J. B. Tingle and H. F. Rolker [*Am. Chem. J.*, **30,** 1889 (1908)] report mp 168°. Some of our samples melted sharply at 219° but in most cases the recorded melting point was registered. Nevertheless all samples gave good analytical data.

cm^{-1}, instead of bands at 3300, 1680–1630, and 1570–1515 cm^{-1}, is a clear indication that the diamide compound has been transformed into one of the two possible imides, usually N-phenylphthalimide. Ultraviolet spectroscopy is less useful since no correlation between absorption bands at 224–230 and 250–260 mμ and structure is apparent.

Acknowledgment.—The authors gratefully acknowledge a grant (1222) from the National Research Council of Argentina and a scholarship awarded to one of them (E. G. D. de T.). They thank Mrs. B. B. de Deferrari and Mr. Charles Beazley for the microanalyses recorded.

Possible Antifertility Compounds. IV.[1] Diphenylnaphtho[1,2-*b*]- and Diphenylnaphtho[2,1-*b*]furans

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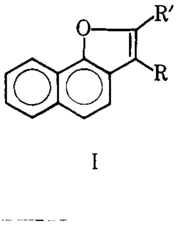
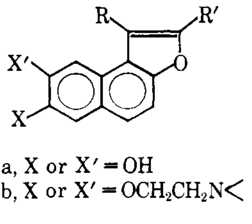
In view of the potent estrogenic activity shown by a large series of phenanthrene compounds, the presence of this nucleus in the steroidal sex hormones and the close resemblance of naphthofuran to phenanthrene, the naphthofurans of type I and II were synthesized (see Tables I and II on the following page).



I



IIa, X or X' = OH
b, X or X' = $OCH_2CH_2N<$

Experimental Section[2]

2,3-Bis(*p*-methoxyphenyl)naphthol[1,2-*b*]furan (1).—α-Naphthol (0.01 mole), *p,p'*-dimethoxybenzoin (0.01 mole), freshly distilled peroxide-free dioxane (30 ml), and concentrated HCl (10 ml) were refluxed for 24 hr. The solution was poured into water, the oily layer was taken up in ether, and the ethereal layer which exhibited a blue-violet fluorescence was washed with 1% NaOH until the alkaline layer was colorless and finally with water. Sufficient petroleum ether (bp 60–80°) was added to the dried clear ethereal solution, and the yellowish solid which separated out was filtered. Two recrystallizations from hot petroleum ether yielded the pure compound, mp 120–121°, yield 29.6%.

Anal. Calcd for $C_{26}H_{20}O_3$: C, 82.12; H, 5.26. Found: C, 81.02; H, 5.18.

7-Hydroxy-1,2-bis(*p*-methoxyphenyl)naphtho[2,1-*b*]furan (5) was prepared from 2,6-dihydroxynaphthalene and *p,p'*-dimethoxybenzoin as described above. In this case the ethereal extract was treated with 8% NaOH, and the alkaline extract was acidified. The separated product on isolation with ether and subsequent treatment with petroleum ether gave a dark oily material. The granular crystals which separated out from the oil after 2–3 days, on recrystallization from benzene–petroleum ether, gave pure **5**, mp 167°, yield 67%.

Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.80; H, 5.04. Found: C, 78.70; H, 5.57.

Dialkylaminoethyl Ethers (IIb) of Substituted Diphenylnaphtho[2,1-*b*]furans (IIa).—A mixture of the appropriate dialkylaminoethyl chloride hydrochloride (0.001 mole), hydroxynaphthofuran (0.001 mole), freshly dried K_2CO_3 (1 g), and acetone (25 ml) was refluxed for 24 hr. After removal of acetone, the mixture was treated with warm water and cooled, and the solid which separated out was filtered and recrystallized from aqueous acetone.

Acknowledgment. Thanks are due to Professor A. B. Sen for his interest in the present work. One of the authors (S. C. S.) is grateful to the Council of Scientific and Industrial Research, New Delhi, for the grant of a junior research fellowship.

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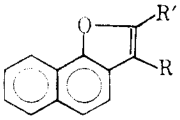
(1) Part III: S. S. Tiwari and S. C. Srivastava, *J. Indian Chem. Soc.*, **44,** 421 (1967).

(2) Melting points were taken in capillary tubes and are uncorrected.

Table I

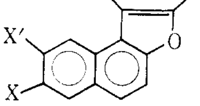
2,3-Bis(alkoxyphenyl)naphtho[1,2-*b*]furans

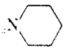
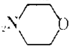
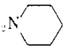
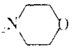
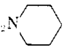
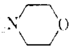
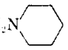
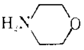
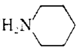
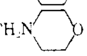


No.	R	R′	Yield, %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
2	*o*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	20.5	113–115	$C_{26}H_{20}O_3$	82.12	5.26	81.34	5.60
3	*o*-$OCH_3C_6H_4$	*o*-$OCH_3C_6H_4$	26	125	$C_{26}H_{20}O_3$	82.12	5.26	81.42	5.36
4	3,4-$CH_2O_2C_6H_3$	3,4-$CH_2O_2C_6H_3$	25	125	$C_{26}H_{16}O_5$	76.49	3.91	76.28	4.5

Table II

7- and 8-Hydroxy- and Dialkylaminoalkoxy-1,2-bis(alkoxyphenyl)naphtho[2,1-*b*]furans



No.	X	X′	R	R′	Yield, %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
6	$OCH_2CH_2N(C_2H_5)_2$	H	*p*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	90	101–102	$C_{32}H_{33}NO_4$			2.82			2.75
7	OCH_2CH_2N 	H	*p*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	92	99	$C_{33}H_{33}NO_4$			2.75			2.71
8	OCH_2CH_2N 	H	*p*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	92	87–88	$C_{32}H_{31}NO_5$			2.74			2.81
9	OH	H	*o*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	65	178	$C_{26}H_{20}O_4$	78.80	5.04		79.11	5.12	
10	$OCH_2CH_2N(C_2H_5)_2$	H	*o*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	88	96	$C_{32}H_{33}NO_4$			2.82			2.73
11	OCH_2CH_2N 	H	*o*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	90	88–89	$C_{33}H_{33}NO_4$			2.75			2.78
12	OCH_2CH_2N 	H	*o*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	84	96–97	$C_{32}H_{31}NO_5$			2.74			2.79
13	OH	H	*o*-$OCH_3C_6H_4$	*o*-$OCH_3C_6H_4$	70	183–184 dec	$C_{26}H_{20}O_4$	78.80	5.04		78.34	5.21	
14	$OCH_2CH_2N(C_2H_5)_2$	H	*o*-$OCH_3C_6H_4$	*o*-$OCH_3C_6H_4$	86	91–92	$C_{32}H_{33}NO_4$			2.82			2.78
15	OCH_2CH_2N 	H	*o*-$OCH_3C_6H_4$	*o*-$OCH_3C_6H_4$	90	88–89	$C_{33}H_{33}NO_4$			2.75			2.79
16	OCH_2CH_2N 	H	*o*-$OCH_3C_6H_4$	*o*-$OCH_3C_6H_4$	92	90	$C_{32}H_{31}NO_5$			2.74			2.65
17	H	OH	*p*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	67	142–144	$C_{26}H_{20}O_4$	78.80	5.04		78.41	5.1	2.79
18	H	$OCH_2CH_2N(C_2H_5)_2$	*p*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	84	92	$C_{32}H_{33}NO_4$			2.82			
19	H	OCH_2CH_2N 	*p*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	89	94–95	$C_{33}H_{33}NO_4$			2.75			2.79
20	H	OCH_2CH_2N 	*p*-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4$	91	87–88	$C_{32}H_{31}NO_5$			2.74			2.81
21	H	OH	*o*-$OCH_3C_6H_4$	*o*-$OCH_3C_6H_4$	63	173–175	$C_{26}H_{20}O_4$	78.80	5.04		78.71	5.01	
22	H	$OCH_2CH_2N(C_2H_5)_2$	*o*-$OCH_3C_6H_4$	*o*-$OCH_3C_6H_4$	90	100–101	$C_{32}H_{33}NO_4$			2.82			2.80
23	H	OCH_2CH_2N 	*o*-$OCH_3C_6H_4$	*o*-$OCH_3C_6H_4$	85	110–111	$C_{33}H_{33}NO_4$			2.75			2.78
24	H	OCH_2CH_2N 	*o*-$OCH_3C_6H_4$	*o*-$OCH_3C_6H_4$	82	96	$C_{32}H_{31}NO_5$			2.74			2.82

Some 2-Aryl-5-nitrobenzimidazole 3-Oxides

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Received April 10, 1967

Derivatives of benzimidazole are of interest as potential antimetabolites. The synthesis of some 2-aryl-5-nitrobenzimidazole 3-oxides is reported here.[2] The starting material, 4-nitro-2-nitrosoaniline,[3] was prepared by an improved procedure.

Experimental Section[4]

4-Nitro-2-nitrosoaniline.[3]—DL-Alanine (8.9 g) and Na_2CO_3 (20.0 g) in water (400 ml) were stirred at 40° with fluoro-2,4-dinitrobenzene (12.0 ml) for 2 hr, and the clear solution of N-(2,4-dinitrophenyl)alanine was diluted to 8 l. with 5% (w/v) aqueous $NaHCO_3$. The diluted solution[5] was photolyzed in 1-l. portions in a standard Hanovia 1-l. photochemical reactor[6] at room temperature for 16 hr while being stirred vigorously both with a magnetic stirrer and with a brisk flow of air to remove the acetaldehyde formed. The product [12.7 g, λ_{max} 284, 348 mμ (ϵ 15,100, 11,200)] was filtered off, washed well with water, and dried at 110°. It was obtained as a green crystalline powder, mp 183–186°, sufficiently pure for further use.

2-Aryl-5-nitrobenzimidazole 3-Oxides.—A solution of 4-nitro-2-nitrosoaniline (2 mmoles) and the appropriate aldehyde (2.2

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(1) Biochemistry Department, Dalhousie University, Halifax, Nova Scotia, Canada.

(2) For a preliminary report see D. W. Russell, *Chem. Commun.*, 498 (1965).

(3) D. W. Russell, *J. Chem. Soc.*, 894 (1963).

(4) Melting points were determined on a hot stage and are corrected. Microanalyses were by Dr. F. Pascher, Bonn, West Germany.

(5) To each 1 l. of solution, 0.3 g of finely powdered, recrystallized 4-nitro-2-nitrosoaniline[3] was added before photolysis. This acted as a seed and prevented deposition of the reaction product upon the glass surfaces of the reaction vessel. The amount added was subtracted in calculating the yield.

(6) Engelhard Hanovia Lamps, Bath Road, Slough, Bucks, England.