228.5°), 10 ml. of *o*-dichlorobenzene, and 16.0 g. of copper powder was stirred and heated under reflux to 150–160° and held there for 4 hr. The cooled, dark brown reaction product was transferred to a Soxhlet thimble and extracted with 700 ml. of chlorobenzene for 16 hr. Upon cooling, the chlorobenzene solution deposited 10.10 g. of V (70% yield), m.p. 345–349°. Two recrystallizations from chlorobenzene gave bright yellow plates, m.p. 347–349°.

Anal. Calcd. for $C_{42}H_{24}N_2O_6$: C, 77.45; H, 3.71; N, 4.30; O, 14.72. Found: C, 76.70; H, 3.61; N, 4.25; O, 14.60.

8,8'-Diamino-1,1'-bianthraquinonyl (VI) was obtained from the dibenzamido compound (V) by warming it with concentrated sulfuric acid at 100°. The crude product was crystallized twice from chlorobenzene, giving an 84% yield of shiny red plates, m.p. >350°.

Anal. Calcd. for $C_{28}H_{16}N_2O_4$: C, 75.66; H, 3.63; N, 6.30; O, 14.40. Found: C, 74.80; H, 3.60; N, 6.42; O, 13.90.

10,10'-Dipyrazolanthronyl (VII). A solution of 4.66 g. of the diamine (VI) in 50 ml. of concentrated sulfuric acid was converted into the tetrazo derivative by treatment with 1.70 g. of sodium nitrite. The addition of approximately 40 g. of ice caused the diazonium sulfate to precipitate, and this was filtered off and added to a solution of 11.6 g. of sodium bisulfite, 12 g. of ice, 14 ml. of 28% sodium hydroxide, and 14 ml. of water. The resulting suspension was heated to 80° and held there 45 min., during which time a further 18 ml. of 28% sodium hydroxide and 5.0 g. of sodium bisulfite were added. The initial yellow color of the solution changed to red. Then 20 g. of sodium chloride was added and the solution was cooled. The red precipitate was filtered, pressed dry, and added to 75 ml. of 99.5% sulfuric acid at 40–50°. The temperature of the solution was then raised slowly to 90–98°, where it was held for 1.5 hr. Pouring the solution onto ice gave a yellow precipitate, which after filtration, washing, and drying weighed 3.90 g. (85% yield). A sample recrystallized twice from nitrobenzene melted above 350° and had λ_{max} 268 and 300 mμ (ε 20,500 and 24,200).

Anal. Calcd. for $C_{28}H_{14}N_4O_2$: C, 76.70; H, 3.22; N, 12.78. Found: C, 76.20; H, 3.50; N, 12.30.

The *dibenzoyl derivative* (VIII), obtained from VII by treatment with benzoyl chloride in pyridine, crystallized from chlorobenzene in pale yellow plates, m.p. >350°.

Anal. Calcd. for $C_{42}H_{26}N_4O_4 \cdot {}^1/_4C_6H_5Cl$: C, 77.00; H, 4.02; Cl, 1.31; N, 8.28; O, 9.42. Found: C, 77.30; H, 3.49; Cl, 1.62; N, 8.42; O, 9.50.

10-Chloropyrazolanthrone. The reaction of 1-chloro-8-nitroanthraquinone (m.p. 263°) with hydrazine hydrate in pyridine yielded a purple solid which was triturated with 10% sodium hydroxide solution and filtered. Acidification of the basic filtrate gave a light yellow solid, which was crystallized from *o*-dichlorobenzene, giving a 71% yield of the known 10-chloropyrazolanthrone, m.p. 346–347° (lit. 346–347°[5]; >360°[3]), identified by comparison of melting point and infrared spectrum with those of an authentic sample.

1-Amino-8-nitroanthraquinone. 1-Chloro-8-nitroanthraquinone was treated with *p*-toluenesulfonamide, sodium acetate, and cuprous chloride in boiling amyl alcohol, giving a 95% yield of crude 1-toluenesulfonamido-8-nitroanthraquinone. A sample after crystallization from acetic acid melted at 255.0–256.5°. This tosyl derivative was hydrolyzed in 81% yield to the amine by warming it in concentrated sulfuric acid for a few minutes, and pouring the resulting solution into water. Crystallization from *o*-dichlorobenzene gave red needles, m.p. 298–299° (dec.) (lit. 294°[6] and 283–284°[7]).

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N-Substituted Imides. II. Potassium Naphthalimide as a Reagent for the Identification of Alkyl Halides[1]

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Many reagents have been suggested for the identification of alkyl halides.[4] Recent studies have included *N*-substituted phthalimides[5] and saccharins.[6] Continuing work in this laboratory concerned with *N*-substituted imides possessing physiological activity suggested that potassium naphthalimide might be a satisfactory reagent for this purpose.

The derivatives were prepared by condensing potassium naphthalimide and the appropriate alkyl halide using dimethylformamide as solvent. The reaction went smoothly for primary and secondary chlorides, bromides, and iodides but yields were low with the secondary halides. Tertiary halides did not react.

The crude products were recrystallized from various alcohols or alcohol-water mixtures. In each case a white crystalline solid with a sharp melting point was obtained. Attempts to determine saponification equivalents were unsuccessful as the imide linkage resisted all attempts at hydrolysis.

Although the melting points of the products (Table I) were close together in the higher members of the series, all were solids and could be used as derivatives. Only *N*-methyl- and *N*-ethyl naphthalimide have been previously reported.[7]

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TABLE I[a]

N-ALKYLNAPHTHALIMIDES

N-Alkyl Substituent	Yield,[b] %	M.P.	Solvent[c]	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Methyl	92	206.5[d]	A	$C_{13}H_9NO_2$		
Ethyl	88	154[e]	A	$C_{14}H_{11}NO_2$		
Propyl	90	158–159	B	$C_{15}H_{13}NO_2$	5.86	6.14
Isopropyl	12	163–164	C	$C_{15}H_{13}NO_2$	5.86	5.63
Butyl	95	96.5–97	B	$C_{16}H_{15}NO_2$	5.53	5.27
sec-Butyl	4	111–112	C	$C_{16}H_{15}NO_2$	5.53	5.43
Amyl	55	86	C	$C_{17}H_{17}NO_2$	5.24	5.10
Isoamyl	57	104–105	C	$C_{17}H_{17}NO_2$	5.24	5.11
1-Methylbutyl	4	69	D	$C_{17}H_{17}NO_2$	5.24	5.50
Hexyl	75	81.5–82.5	B	$C_{18}H_{19}NO_2$	4.97	5.24
Heptyl	90	70.5–71.5	C	$C_{19}H_{21}NO_2$	4.74	4.79
Octyl	43	42.5–43.5	A	$C_{20}H_{23}NO_2$	4.52	4.50
Nonyl	95	56.5–57	C	$C_{21}H_{25}NO_2$	4.33	4.01
Decyl	95	52	A	$C_{22}H_{27}NO_2$	4.19	4.29
Undecyl	80	53–53.5	C	$C_{23}H_{29}NO_2$	3.98	3.99
Dodecyl	95	56–57	E	$C_{24}H_{31}NO_2$	3.83	3.85
Benzyl	82	95–96	B	$C_{19}H_{13}NO_2$	4.87	5.01

[a] All melting points are corrected. [b] Crude yield based on potassium naphthalimide. [c] Recrystallizing solvent: A = 95% ethanol; B = isopropanol; C = isopropanol-water; D = methanol-water; E = methanol. [d] G. F. Jaubert, *Ber.*, **28**, 360 (1895) reported m.p. 205°. [e] G. F. Jaubert, *op. cit.*, reported m.p. 148°.

EXPERIMENTAL

N-Alkylnaphthalimides. In a small flask fitted with an efficient reflux condenser were placed 2.35 g. (0.01 mol.) of potassium naphthalimide,[8] the appropriate alkyl halide (0.01 mol.), and 15 ml. of dimethyl formamide. The mixture was refluxed on a steam bath for 1 hr. and cooled, and the precipitated potassium bromide was removed by filtration. Cold water was added to the filtrate and the precipitated *N*-alkyl naphthalimide was removed and dissolved in ether. Any ether insoluble material was removed and the ether evaporated to give the crude product which was recrystallized.

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Tetrazole-Azidoazomethine Equilibrium. II. Amino- and Hydroxypyridotetrazoles[1]

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The predicted absence[2] of tetrazole-azidoazomethine tautomerism for derivatives of pyridotetrazole with certain strong electron donating substituents has been established by examination of 6- and 8-hydroxy- and 8-aminopyridotetrazole. On treatment with sodium azide in the presence of hydrochloric acid in refluxing aqueous ethanol, 2-chloro-3-amino- and 2-chloro-3-hydroxypyridine are transformed into 8-amino- (I) and 8-hydroxypyridotetrazole (II) respectively. A similar reaction with 2-chloro-5-aminopyridine occurs with the unexpected replacement of the amino group with the hydroxyl group. It is assumed that the functional group has not migrated to another position

TABLE I

INFRARED ABSORPTION (cm.$^{-1}$) FROM KBr DISKS (% TRANSMITTANCE)

8-Amino-pyridotetrazole (I)	8-Hydroxy-pyridotetrazole (II)	6-Hydroxy-pyridotetrazole (III)
3401 (35.0)	3059 (18.0)	3448 (51.8)
3300 (32.5)	2994 (18.2)	2564 (27.0)
3195 (34.9)	2793 (25.6)	1923 (51.7)
3096 (39.6)	2660 (24.0)	1786 (55.6)
1639 (30.5)	2475 (40.0)	1656 (48.0)
1570 (39.3)	1894 (74.8)	1570 (49.4)
1497 (36.9)	1835 (79.2)	1553 (40.7)
1414 (42.6)	1764 (78.6)	1515 (28.5)
1381 (43.2)	1631 (34.5)	1431 (23.7)
1361 (45.0)	1585 (6.5)	1350 (29.0)
1318 (48.6)	1502 (18.9)	1311 (23.7)
1232 (56.5)	1429 (15.7)	1259 (37.6)
1220 (37.7)	1393 (30.0)	1211 (24.0)
1156 (40.7)	1321 (15.0)	1147 (37.7)
1107 (40.0)	1239 (28.9)	1106 (23.0)
1076 (36.5)	1206 (21.0)	1095 (25.3)
1067 (42.9)	1159 (14.0)	1028 (41.5)
938 (50.0)	1104 (34.3)	964 (49.0)
841 (39.0)	1067 (45.4)	873 (27.6)
716 (28.0)	1044 (47.2)	815 (19.4)
701 (46.5)	1016 (24.6)	793 (26.5)
693 (47.4)	952 (71.0)	768 (32.4)
	880 (44.5)	696 (46.4)
	849 (68.7)	
	794 (44.0)	
	774 (26.0)	
	744 (21.3)	
	696 (30.0)	

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