k_1 = association constant for M^+ and Br^- in alkali nitrate phase
k_2 = distribution constant for associated alkali bromide between alkali nitrate phase and silver bromide phase
K_o = experimental value, observed distribution coefficient of total alkali bromide in AgBr phase per calculated bromide ion activity in alkali nitrate phase
K_{OM} = experimental value, observed alkali metal (I) distribution coefficient between AgBr and alkali nitrate
K = distribution constant for reaction: $(M^+ + Br^-)_{MNO_3} \rightarrow (MBr)_{AgBr}$
$K_{(M)}$ = K for M solute
$K_{(M')}$ = K for M' solvent
(Br) = experimental value, total bromide in alkali nitrate-AgBr
$[Br^-]$ = calculated bromide ion activity in alkali nitrate phase
$(MBr + M'Br)_{AgBr}$ = experimental value, total alkali bromide concentration in AgBr phase = $(Br)_{AgBr}$
$(M)_{M'NO_3}$ = experimental value, alkali metal (I) concentration in $M'NO_3$ phase by flame photometry
$(M)_{AgBr}$, $(M')_{AgBr}$ = experimental value, alkali metal (I) concentration in AgBr phase by flame photometry
$[M^-]$ = activity of alkali metal ion in alkali nitrate phase
$[MBr]_{M'NO_3}$ = activity of associated MBr in $M'NO_3$ phase
$[MBr]_{AgBr}$ = activity of alkali bromide in AgBr phase, assumed equal to $(M)_{AgBr}$

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Condensation of Some Aromatic Amines with Phenyl Glyoxal

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SOME NEW ANILS have been prepared by condensing phenyl glyoxal hydrate (*1*) with aniline, *p*-chloroaniline, *o*-, and *p*-nitroanilines, *o*-, and *p*- toluidines, and *α*-, and *β*-naphthylamines. They have been characterized by preparing their *p*- nitrophenyl hydrazones, 2,4-dinitrophenyl hydrazones, semicarbazones, and oximes. The oximes give color reactions with a number of metal ions and offer the possibility of being used as analytical reagents.

EXPERIMENTAL

Preparation of Anils. Equimolar quantities of phenyl glyoxal hydrate and the corresponding amines in 95% ethanol were refluxed on a water bath. The solid products, which separated on cooling, were crystallized from absolute alcohol and gave anils listed in Table I. These anils are soluble in methanol, ethanol, benzene, acetone, and chloro-

Table I. Anils Derived from Phenyl Glyoxal and Aromatic Amines

Anil	Color	Formula	M.P., ° C.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found
R-[a]Aniline	Yellow	$C_{14}H_{11}ON$	89–90	90.9	6.69	6.73
R- *p*-Chloroaniline[b]	Colorless	$C_{14}H_{10}ONCl$	115–116	63.6	5.74	5.89
R- *o*-Nitroaniline	Yellow	$C_{14}H_{10}O_3N_2$	105–106	82.2	11.02	11.29
R- *p*-Nitroaniline	Yellow	$C_{14}H_{10}O_3N_2$	127–129	47.2	11.02	11.41
R- *o*-Toluidine	Reddish brown	$C_{15}H_{13}ON$	Gummy mass	85.5	6.28	6.12
R- *p*-Toluidine	Yellow	$C_{15}H_{13}ON$	97–98	89.6	6.28	6.32
R- *α*-Naphthylamine[b]	Yellow	$C_{18}H_{13}ON$	136–137	92.2	5.40	5.24
R- *β*-Naphthylamine[b]	Yellow	$C_{18}H_{13}ON$	90–91	61.8	5.40	5.12

[a] R = C_6H_5—CO—CH= (phenacylidene radical). [b] No warming necessary to obtain these anils.

Table II. Characteristics of the Derivatives of Anils

Anil	*p*-Nitro Phenyl Hydrazones M.P., ° C.	*p*-Nitro Phenyl Hydrazones Nitrogen, % Calcd.	*p*-Nitro Phenyl Hydrazones Nitrogen, % Found	2,4-Dinitro Phenyl Hydrazones M.P., ° C.	2,4-Dinitro Phenyl Hydrazones Nitrogen, % Calcd.	2,4-Dinitro Phenyl Hydrazones Nitrogen, % Found	Semicarbozones M.P., ° C.	Semicarbozones Nitrogen, % Calcd.	Semicarbozones Nitrogen, % Found	Oximes M.P., ° C.	Oximes Nitrogen, % Calcd.	Oximes Nitrogen, % Found
R-[a] Aniline	185–186	16.28	16.53	236–238	17.99	17.74	190–191	21.05	20.95	58–59	12.5	12.46
R- *p*-Chloroaniline	200–201	16.16	16.46	267–269	16.52	16.46	180–181	18.63	18.44	146–147	10.83	10.35
R- *o*-Nitroaniline	233–234	17.99	17.61	255–256	19.35	19.12	197–198	22.50	22.31	189–201	15.61	15.42
R- *p*-Nitroaniline	250–252	17.99	17.54	262–263	19.35	19.40	203–205	22.50	22.25	206–207	15.61	15.48
R- *o*-Toluidine	100–101	15.64	15.56	250–251	17.36	17.25	. . .	. . .	. . .	77–78	11.76	11.56
R- *p*-Toluidine	134–135	15.64	15.32	263–265	17.36	17.16	244–245	20.00	19.95	101–102	11.76	11.43
R- *α*-Naphthylamine	264–265	14.21	14.13	194–195	15.94	15.63	210–211	17.72	17.56	119–120	10.22	10.20
R- *β*-Naphthylamine	189–190	14.21	14.09	247–249	15.94	15.83	100–101	17.72	17.43	95–96	10.22	10.32

[a] R = C_6H_5—CO—CH=.

form, producing a light yellow coloration, while they are insoluble in water and petroleum ether.

Derivatives of Anils. *p*- Nitrophenyl hydrazones, 2,4-dinitrophenyl hydrazones, semicarbazones, and the oximes of the above anils were prepared by the usual methods. These derivatives were crystallized from absolute alcohol except the *p*- nitrophenyl hydrazone of *o*- toluidine which could be crystallized from methanol. The yield of the derivatives was almost quantitative. The characteristics of the above derivatives are given in Table II.

The oximes give color reactions with alcoholic solution of heavy metal ions, especially copper, cobalt, nickel, and iron (ic). The colors are all green of varying shades ranging from yellow green (nickel), to bright green (copper) and dark green (cobalt). With ferric ions color response is given by only two of the above oximes—*viz.*, phenacylidene β-naphthylamine and phenacylidene *o*- toluidine oximes which give reddish orange and violet colors.

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Chemistry of Imidoyl and Amide Chlorides

On the Preparation and Properties of *N*-Substituted 2-Furimidoyl Chlorides. *N,N'*-Disubstituted 2-Furamidines

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N-Monosubstituted-2-furamides C_4H_9O—CONHR, where R = aryl or *n*-C_3H_7—, *n*-C_4H_9—, or $C_6H_5CH_2$—, on reaction with PCl_5 gave new imidoyl chlorides, C_4H_3—C(Cl)=NR; with R = CH_3—, C_2H_5—, and *iso*-C_3H_7—, however, amide chlorides, C_4H_3O—CCl_2NHR, subsequently convertible to imidoyl chlorides, were obtained; with R = *tert*-C_4H_9—, the alkyl group was eliminated to form 2-furonitrile and *tert*-butyl chloride. The new imidoyl chlorides were converted with primary amines to a number of new *N,N'*-disubstituted-2-furamidines and their salts.

ALTHOUGH a large number of imidoyl chlorides have been prepared (*3, 15*), the present paper reports the first isolation and characterization of such derivatives obtained from *N*-substituted amides of 2-furoic acid.

Depending upon the nature of the *N*-substituent in the 2-furamide, the product of the reaction with phosphorus pentachloride may be either the imidoyl or the amide chloride (*9*), or fragmentation products.

The eleven *N*-arylimidoyl chlorides (I–XI) were obtained in good yield, either as viscous yellow oils or as crystalline solids. The reaction between *N*-alkyl-2-furamides and PCl_5, however, does not follow the same pattern. Thus, *N*-(*n*-propyl)- and *N*-(*n*-butyl)-2-furamides reacted with evolution of hydrogen chloride yielding the imidoyl chlorides (XIV, XVI), but *N*-methyl-, *N*-ethyl-, and *N*-isopropyl-2-furamides reacted without evolution of hydrogen chloride to yield the amide chlorides. The amide chlorides, similar to the ones reported previously (*3, 9*), were extremely sensitive to moisture and not isolable in a pure state. Heating of the amide chlorides in dry benzene resulted in the imidoyl chlorides (XII, XIII, XV). Dry pyridine can be used in place of benzene with the same result.

N-alkyl-2-furimidoyl chlorides are thermally less stable and more sensitive than the *N*-aryl analogs. The ease of thermal decomposition on varying the nature of the alkyl group increases in the order prim. < sec. < tert.

Consistent with the results of Degnan and Pope (*8*) is the authors' observation that the reaction of *N*-*tert*-butyl-2-furamide with PCl_5 gives 2-furonitrile and *tert*-butyl chloride, presumably by immediate decomposition of the unstable intermediate imidoyl chloride. This can be rationlized in terms of a considerable fragmentation effect of the *tert*-butyl group. The instability of *N*-phenylsulfonyl-2-furimidoyl chloride, which spontaneously decomposes into furonitrile and benzenesulfonyl chloride, may also be noted. This had not been anticipated since the corresponding *N*-phenylsulfonylimidoyl chlorides of other aliphatic and aromatic counterparts are very stable (*4*).

Existence of any syn-anti equilibria in the prepared imidoyl chlorides, otherwise found in sterically similar compounds (*11, 13*), was not apparent. A recent attempt to detect the presence of syn-anti isomers of imidoyl chlorides indicated only the presence of anti isomers (*10*). This appears to be consistent with the stereochemistry of imidoyl chlorides prepared from oximes (*7*).

In addition to direct identification, all the imidoyl chlorides were converted to *N,N'*-disubstituted-2-furamidines (*8, 12*). Contrary to Degnan and Pope's observation (*8*), *N*-aryl-2-furamides can be converted to *N*-aryl-*N'*-alkyl-2-furamidines via the imidoyl chlorides in the presence of an alkyl amine. In this case, however, a considerable excess of the alkyl amine has to be used.

The experimental results obtained are presented in Tables I and II. All melting points are uncorrected. Crystalline

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