intermediate between the benzal- and benzylacetones in agreement with previous reports (*15, 16, 30*). The ketones containing a nitro substituent on the phenyl ring gave two strong bands in the 1520 and 1345 cm^{-1} regions while those bearing a nitrile group exhibited the characteristic strong absorption band at 2225 cm^{-1}.

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Reaction of Hydroxylamine with Reissert Compounds

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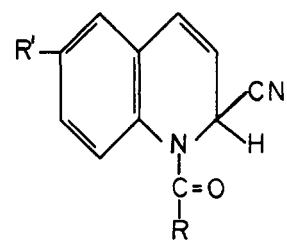
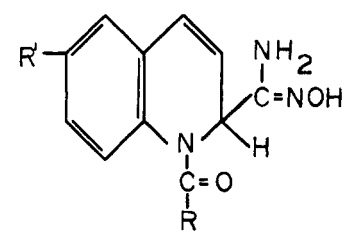
Some new amidoximes have been prepared from Reissert compounds, and the unusual acid-catalyzed hydrolysis of these amidoximes has been studied.

A previous paper (*10*) reported the reaction of 1-benzoyl-1,2-dihydroquinaldonitrile (I, R = C_6H_5; R′ = H) with hydroxylamine to give 1-benzoyl-1,2-dihydroquinaldamidoxime (II, R = C_6H_5; R′ = H). Acid-catalyzed hydrolysis of this product gave an unusual result—benzaldehyde was obtained along with the expected benzoic acid much as benzaldehyde was formed by the acid-catalyzed hydrolysis of Reissert compounds (I, R = C_6H_5; R′ = H and III, R = C_6H_5) (*2, 9*).



I



II

Several new amidoximes listed in Table I have been prepared by the reaction of hydroxylamine with the appropriate Reissert compound.

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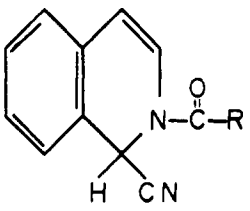
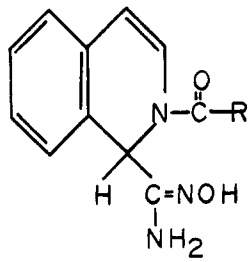
Table I. Amidoximes

	Amidoxime	Reissert cpd used	Yield, %	Mp, °C[a, b]	R_f amidoxime	R_f Reissert cpd	Molecular formula	Analyses[c] of amidoximes Calcd	Found
1.	II, R=*o*—Cl—C_6H_4; R′=H	I, R=*o*—Cl—C_6H_4; R′=H[d]	93	174–175	0.55	0.72	$C_{17}H_{14}ClN_3O_2$	C, 62.29 H, 4.30 N, 12.82 Cl, 10.82	C, 62.24 H, 4.21 N, 12.61 Cl, 10.61
2.	II, R=CH_3; R′=H	I, R=CH_3; R′=H[e]	63	169–171	0.45	0.65	$C_{12}H_{13}N_3O_2$	C, 62.30 H, 5.67 N, 18.18	C, 62.25 H, 5.50 N, 17.97
3.	II, R=C_6H_5; R′=CH_3	I, R=C_6H_5; R′=CH_3[f]	93	158–160	0.56	0.62	$C_{18}H_{17}N_3O_2$	C, 70.36 H, 5.57 N, 13.67	C, 70.22 H, 5.66 N, 13.90
4.	II, R=C_6H_5; R′=CH_3—O	I, R=C_6H_5; R′=CH_3—O[f]	88	149–150	0.54	0.67	$C_{18}H_{17}N_3O_3$	Reported[g] mp 148–149° C	
5.	IV, R=C_6H_5	III, R=C_6H_5[h]	91	182–183	0.51	0.52	$C_{17}H_{15}N_3O_2$	C, 69.62 H, 5.17 N, 14.33	C, 69.55 H, 5.22 N, 14.08
6.	IV, R=CH_3	III, R=CH_3[e]	93	194–196	0.42	0.62	$C_{12}H_{13}N_3O_2$	C, 62.30 H, 5.67 N, 18.18	C, 62.60 H, 5.63 N, 18.32

[a] All melting points were taken in capillaries and are corrected. [b] Recrystallized from ethanol. [c] Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [d] Lit. (*5, 8*). [e] Lit. (*8*). [f] Lit. (*7*). [g] Lit. (*4*). [h] Lit. (*6*).



III



IV

Each of the amidoximes was subjected to acid-catalyzed hydrolysis under various conditions. These included the use of 10% hydrochloric acid (*2, 9, 10*), concentrated hydrochloric acid and 2,4-dinitrophenylhydrazine (*2, 10*), and 48% hydrobromic acid (*3*) and 2,4-dinitrophenylhydrazine. The results of the acid-catalyzed hydrolysis reactions are summarized in Table II. The quinoline or isoquinoline components of the hydrolysis products were isolated only in the cases noted in the table.

In the cases of the amidoximes prepared from quinoline or 6-substituted quinoline Reissert compounds and where R is phenyl, benzaldehyde was obtained. Substitution of chlorine in the ortho position of the benzene ring of the benzoyl group (II, R=*o*—Cl—C_6H_4; R′=H) caused the yield to drop considerably. The amidoxime (IV, R=C_6H_5) prepared from isoquinoline Reissert compound was found to be more resistant to hydrolysis than the corresponding amidoxime prepared from quinoline Reissert compound. However, use of 10% hydrochloric acid gave benzaldehyde. Replacement of the benzoyl group by an acetyl group in the amidoximes (II, R=CH_3; R′=H and IV, R=CH_3) failed to yield any trace of aldehyde.

Table II. Acid-Catalyzed Hydrolysis of Amidoximes

Amidoxime	Method	Yield, % Time, hr	R—CHO[a]	R—COOH
1.	A	2	6[b]	81[c, d]
2.	B	2	None	[e]
3.	B	2	41[f]	32[g]
4.	B	2	37[f]	51[g]
5.	A	2	16[f]	52[g, h]
5.	C	2	28[f]	25[g, i]
6.	B	2	None	[e]

[a] Identified as the 2,4-dinitrophenylhydrazone. [b] Mp 205–206°d. [c] Mp 139–140°. [d] Yield of quinoline was 25% identified as its picrate, mp 201–203°; yield of quinaldic acid 65%, mp 156–157°. [e] Strong odor of acetic acid. [f] Mp 237–238°. [g] Mp 121–122°. [h] Yield of isoquinoline was 10% identified as its picrate, mp 220–222°; yield of isoquinaldic acid was 49%, mp 159–160°. [i] Yield of isoquinoline was 4% identified as its picrate, mp 220–222°; yield of isoquinaldic acid was 42%, mp 159–160°.

EXPERIMENTAL

Amidoximes. The amidoximes were prepared from the appropriate Reissert compound as previously described (*4, 10*). The infrared spectra of the amidoximes (potassium bromide pellet, 1.5 mg/300 mg) was characteristic of amidoximes with peaks at 3350 and 3470 cm^{-1} (NH_2 stretching), a broad band between 2600 and 3300 cm^{-1} (associated OH and NH stretching), a sharp peak between 1640 and 1670 cm^{-1} (C=N), and a peak between 1565 and 1590 cm^{-1} (NH_2) (*1*).

For the subsequent hydrolysis reactions, each sample of amidoxime was recrystallized to a constant melting point and its purity checked by thin layer chromatography (*10*). The R_f values of the amidoximes and their parent Reissert compounds can be found in Table I.

Acid-Catalyzed Hydrolysis Reactions. The acid-catalyzed hydrolysis reactions were carried out as previously described (*10*) using 10% hydrochloric acid (Method A) and concentrated hydrochloric acid and 2,4-dinitrophenylhydrazine (Method B). The hydrolysis reaction using 48% hydrobromic acid and 2,4-dinitrophenylhydrazine (Method C) was carried out exactly as Method B with the exception that 125 ml of 48% hydrobromic acid was substituted for the concentrated hydrochloric acid.

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Improved Synthesis of Arylguanamines

Reaction of Aromatic Nitriles with Dicyandiamide in Presence of Sodium Ethoxide

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Several new arylguanamines were prepared by interaction of aromatic nitriles with dicyandiamide in the presence of sodium ethoxide.

In connection with a research program involving the synthesis of triazines (*1, 2, 3, 6*), the synthesis of arylguanamines was reinvestigated. The base-catalyzed reaction of dicyandiamide with alkyl or aryl nitriles for the synthesis of 2,4-diamino-6-alkyl-(or aryl)-1,3,5-triazines (guanamines) under drastic conditions is known (*5, 7*). Steric factors influence this reaction and consequently *o*-tolunitrile fails to give the appropriate guanamine (*5*).

Sodium ethoxide was successfully used as a catalyst. Good yields of arylguanamines were obtained (Table I).

All guanamines obtained exhibit characteristic infrared absorption bands at 3 to 3.2 microns for amino groups and bands of strong intensity at 6.1 to 6.3 microns for C=C and C=N.

Other distinguishing bands peculiar to each structure are present. Known compounds had spectra identical with those of authentic samples prepared by other methods (*5, 7*).

The NMR spectrum for each compound is in agreement with that predicted for the protons of the group characteristic of the particular structure. NMR data are tabulated in Table I.

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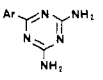
Table I. Arylguanamine Yields



Ar[a]	M.P., °C.	Yield, %	NMR Chemical Shift (δ), P.P.M. NH_2 protons	NMR Chemical Shift (δ), P.P.M. Aromatic protons
C_6H_5	228[b]	27	6.65	7.6-7.75
o-FC_6H_4	247	21	6.50	7.10
m-FC_6H_4	249	66	6.50	7.15-7.8
p-FC_6H_4	249	69	6.55	7.3-8.1
o-ClC_6H_4	232	65	6.50	7.0
m-ClC_6H_4	277	80	6.62	6.4-8.0
p-ClC_6H_4	251[c]	79	6.50	7.3-8.07
o-BrC_6H_4	249	67	6.50	7.25-
m-BrC_6H_4	233	78	6.50	7.25-7.8
p-BrC_6H_4	264	71	6.50	7.2-8.0
o-$CH_3C_6H_4$	202	9	6.50	7.2-8.0
p-$CH_3C_6H_4$	244[d]	27	6.60	7.0-8.0
o-$CF_3C_6H_4$	233	50	6.50	7.4
m-$CF_3C_6H_4$	210	86	6.50	7.4-8.2

[a] C, H, and N analyses for compounds submitted to review and are in accord with theory. [b] (*5*) 226°. [c] (*4*) 226-27°. [d] (*4*) 252-53°. [e] (*6*) 240°.

EXPERIMENTAL

Melting points were taken on a Kofler hot-stage microscope and are uncorrected. The infrared spectra were determined with a Leitz Model III spectrograph, using potassium bromide disks. The NMR spectra were determined on a Varian A 60 A instrument at room temperature in dimethylsulfoxide, using TMS as standard.

2,4-Diamino-6-aryl-1,3,5-triazines (Arylguanamines). In all cases 0.01 mole of arylnitrile and 0.02 mole of dicyandiamide in sodium ethoxide solution (prepared by dissolving 0.015 atom of sodium in 35 ml of absolute ethanol were refluxed for 15 hours. The solution obtained was diluted with water and neutralized with acetic acid. The guanamines precipitated were recrystallized from alcohol or dioxane.

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