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Condensation of Aromatic Nitro Compounds with Arylacetonitriles

V. Some Reactions of Arylcyanomethylenequinone Oximes

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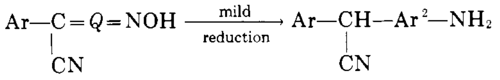
Mild chemical and catalytic reduction convert the arylcyanomethylenequinone oximes to *p*-aminoarylarylacetonitriles. The amino-nitrile compounds are readily hydrolyzed to the corresponding amino-acids. More vigorous catalytic reduction converts the arylcyanomethylenequinone oximes to *p*-aminoarylarylethylamines. There is described the preparation and characterization of many new amino-compounds which would be difficult to prepare by other methods.

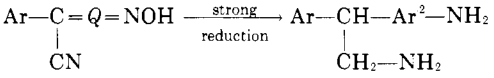
THIS REPORT concerns a continuation of the systematic investigation of the chemical behavior of six representative arylcyanomethylenequinone oximes (*4*), which are more properly named, 4-oxo-α-aryl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oximes. The arylcyanomethylenequinone oximes are reduced to the corresponding *p*-aminoarylarylacetonitriles in good yield using zinc and acetic acid in methanol and some water, or hydrogen and Raney nickel in methanol. The mild reduction of the arylcyanomethylenequinone oximes, which apparently involves an initial 1,6-addition of hydrogen to the *p*-quinoid system, similar to the reduction of fuchsone (*3*), can be represented by the following general equation in which *Q* signifies a *p*-quinoid structure and Ar^2 signifies a *p*-bivalent aromatic radical having the same chemical formula and arrangement of substituents as *Q*.



$$\underset{\displaystyle CN}{\text{Ar—C}}=Q=\text{NOH} \xrightarrow[\text{reduction}]{\text{mild}} \underset{\displaystyle CN}{\text{Ar—CH}}\text{—Ar}^2\text{—NH}_2$$

As part of the proof of structure of the *p*-aminoarylarylacetonitriles, *p*-aminophenylphenylacetonitrile and *p*-aminophenyl-*p*-chlorophenylacetonitrile were independently synthesized by the mild reduction of the corresponding nitro compounds. In addition, the infrared spectra of the mild reduction products possessed characteristic amino group absorption peaks in the 2.8 to 3.0μ region (*2*) and characteristic non-conjugated nitrile group absorption peaks in the 4.47μ region (*5*). The *p*-aminoarylarylacetonitriles were converted to their hydrochloride salts and also to the corresponding amino-acids (*1*) by conventional procedures.

More vigorous reducing conditions using hydrogen and Raney nickel in methanol, converts the arylcyanomethylenequinone oximes to the corresponding *p*-aminoarylarylethylamines.



$$\underset{\displaystyle CN}{\text{Ar—C}}=Q=\text{NOH} \xrightarrow[\text{reduction}]{\text{strong}} \underset{\displaystyle CH_2\text{—}NH_2}{\text{Ar—CH}}\text{—Ar}^2\text{—NH}_2$$

As suggested by other workers (*6, 7*), ammonia may be used in these reactions in order to keep secondary amine formation to a minimum. However, the ammonia must be introduced only after the initial stages of reduction have taken place, otherwise the expected diamines are not produced in good yield.

Table I. Compounds Derived from Arylcyanomethylenequinone Oximes

Compound	M.P.[a]	Yield %	Recrystallization Solvent	Analysis, %[b]
p-Aminophenylphenylacetonitrile	71–72	99[c] 90[d]	Pet. ether[e]	C,80.74; H,5.81; N,13.45 C,80.47; H,5.72; N,13.25
p-Aminophenyl-*p*-chloriphenylacetonitrile	72–73	88[c] 76[d]	Benzene-pet. ether	C,69.27; H,4.57; N,11.54 C,68.96; H,4.59; N,11.52
p-Aminophenyl-*p*-methoxyphenylacetonitrile	134–135	87[c]	Benzene-pet. ether	C,75.60; H,5,92; N,11.76 C,75.71; H,6.07; N,11.66
4-Amino-3-chlorophenylphenylacetonitrile	72–74	96[c]	Benzene-pet. ether	C,69.27; H,4.57; N,11.54 C,69.15; H,4.81; N,11.61
4-Amino-3-methoxyphenylphenylacetonitrile	52–54	81[c]	Pet. ether	C,75.60; H,5.92; N,11.76 C,75.66; H,5.98; N,11.55
4-Amino-3-methylphenylphenylacetonitrile	107–108	96[c] 85[d]	Benzene-pet. ether	C,81.05; H,6.35; N,12.60 C,81.35; H,6.40; N,12.42
p-Aminophenylphenylacetonitrile hydrochloride	218–221	93	Ethanol-ether	Cl,14.49 Cl,14.28
p-Aminophenyl-*p*-chlorophenylacetonitrile hydrochloride	221–223[g]	97	Ethanol-ether	C,60.23; H,4.33; N,10.03 C,59.80; H,4.75; N,10.09
p-Aminophenyl-*p*-methoxyphenylacetonitrile hydrochloride	208–211[g]	94	Ethanol-ether	Cl,12.93 Cl,12.71
4-Amino-3-chlorophenylphenylacetonitrile hydrochloride	187–189[g]	96	Ethanol-ether	Cl,25.41 Cl,25.07
4-Amino-3-methoxyphenylphenylacetonitrile hydrochloride	212–213[g]	94	Ethanol-ether	C,65.64; H,5.41; N,10.20 C,65.22; H,5.34; N,10.20
4-Amino-3-methylphenylphenylacetonitrile hydrochloride	224–227[g]	93	Ethanol-ether	Cl,13.73 Cl,13.49
p-Aminophenylphenylacetic acid	175–177[g]	78	Benzene-pet. ether	C,73.99; H,5.77; N, 6.16 C,73.76; H,5.63; N, 6.13
p-Aminophenyl-*p*-chlorophenylacetic acid	201–203[g]	81	Methanol-water	C,64.31; H,4.53; N, 5.36 C,64.10; H,4.48; N, 5.23
p-Aminophenyl-*p*-methoxyphenylacetic acid	190–192[g]	78	Water	C,70.02; H,5.88; N, 5.44 C,70.30; H,5.91; N, 5.58
4-Amino-3-chlorophenylphenylacetic acid	163–165	93	Methanol-water	C,64.31; H,4.53; N, 5.36 C,64.10; H,4.68; N, 5.37
4-Amino-3-methoxyphenylphenylacetic acid	139–141	78	Water	C,70.02; H,5.88; N, 5.44 C,70.03; H,5.88; N, 5.40
4-Amino-3-methylphenylphenylacetic acid	147–148	65	Benzene-pet. ether	C,74.66; H,6.27; N, 5.81 C,74.71; H,6.44; N, 5.53
2-*p*-Aminophenyl-2-phenylethylamine	102–103	91	Benzene-pet. ether	C,79.21; H,8.24; N,13.20 C,79.32; H,7.95; N,13.02
2-*p*-Aminophenyl-2-*p*-chlorophenylethylamine dihydrochloride	291–294[g]	62	Ethanol-ethylacetate	C,52.60; H,5.36 C,52.58; H,5.60
2-*p*-Aminophenyl-2-*p*-methoxyphenylethylamine	88–89	88	Benzene-pet. ether	C,74.35; H,7.49; N,11.56 C,74.12; H,7.45; N,11.57
2-(4′-Amino-3′-chlorophenyl)-2-phenylethylamine dihydrochloride hemi-hydrate[f]	212–215[g]	79	Ethanolic HCl	C,51.14; H,5.52; Cl,32.35 C,51.37; H,5.23; Cl,31.87
2-(4′-Amino-3′-methoxyphenyl)-2-phenylethylamine dihydrochloride	213–216[g]	90	Ethanol-benzene	C,57.14; H,6.39 C,57.43; H,6.50
2-(4′-Amino-3′-methylphenyl)-2-phenylethylamine dihydrochloride	254–257[g]	80	Ethanol-benzene	C,60.22; H,6.68 C,60.04; H,6.63

[a] All melting points are uncorrected. [b] Analyses by Midwest Microlab, Inc., Indianapolis, Ind. First series calculated, second found. [c] Prepared by zinc and acetic acid reduction. [d] Prepared by hydrogen and Raney nickel reduction. [e] Petroleum ether, b.p. 60–71°. [f] Distinct hydrates are sometimes known to form (*8*) and at least one other hemihydrate has been previously reported (*9*). [g] Melts with decomposition.

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Condensation of Aromatic Nitro Compounds with Arylacetonitriles

VI. Some Reactions of the Arylcyanomethylenequinone Oximes

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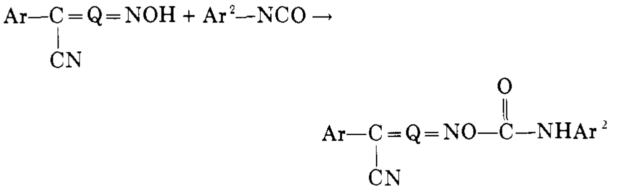
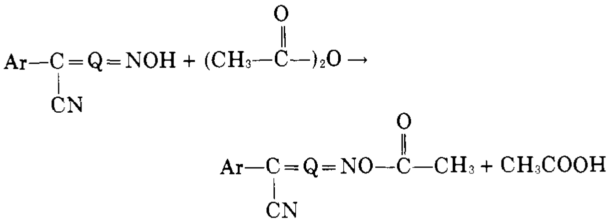
The preparation and characterization of the phenylisocyanate, 1-naphthylisocyanate, acetyl, benzoyl and p-nitrobenzyl derivatives of six arlycyanomethylenequinone oximes are described.

THE PRESENT investigation represents an attempt to prepare some practical derivatives of the arylcyanomethylenequinone oximes which may be useful in the characterization and in the separation of the isomeric forms of the arylcyanomethylenequinone oximes. We have long been aware of the possible isomeric structures of quinone oximes, but we have had little hope of separating such isomers primarily because of the labile hydrogen atom of the oximino group in the quinone oximes. Hence in our investigation of derivatives, we were particularly interested in those in which the labile hydrogen of the oximino group was removed.

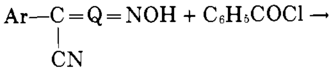
We have successfully prepared the phenylisocyanate (Equation 1), 1-naphthylisocyanate (Equation 1), acetyl (Equation 2), benzoyl (Equation 3), and *p*-nitrobenzyl (Equation 4) derivatives of six representative arylcyanomethylenequinone oximes (*1*).

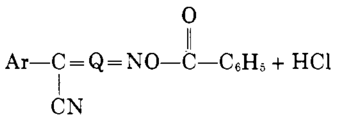


$$\underset{\displaystyle CN}{\underset{|}{Ar{-}C}}{=}Q{=}NOH + Ar^2{-}NCO \rightarrow \underset{\displaystyle CN}{\underset{|}{Ar{-}C}}{=}Q{=}NO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NHAr^2 \quad (1)$$

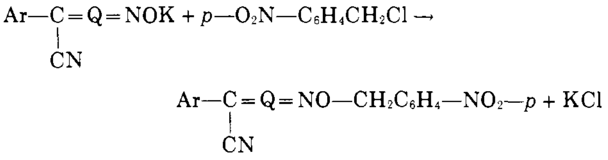


$$\underset{\displaystyle CN}{\underset{|}{Ar{-}C}}{=}Q{=}NOH + (CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-})_2O \rightarrow \underset{\displaystyle CN}{\underset{|}{Ar{-}C}}{=}Q{=}NO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3 + CH_3COOH \quad (2)$$



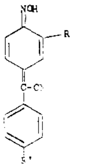


$$\underset{\displaystyle CN}{\underset{|}{Ar{-}C}}{=}Q{=}NOH + C_6H_5COCl \rightarrow \underset{\displaystyle CN}{\underset{|}{Ar{-}C}}{=}Q{=}NO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}C_6H_5 + HCl \quad (3)$$



$$\underset{\displaystyle CN}{\underset{|}{Ar{-}C}}{=}Q{=}NOK + p{-}O_2N{-}C_6H_4CH_2Cl \rightarrow \underset{\displaystyle CN}{\underset{|}{Ar{-}C}}{=}Q{=}NO{-}CH_2C_6H_4{-}NO_2{-}p + KCl \quad (4)$$

The six arylcyanomethylenequinone oximes used in the investigation can be identified by the following schematic index (*1*):



I. $R,R^2{=}H$
II. $R{=}H,R^2{=}Cl$
III. $R{=}H,R^2{=}OCH_3$
IV. $R{=}Cl,R^2{=}H$
V. $R{=}OCH_3, R^2{=}H$
VI. $R{=}CH_3, R^2{=}H$

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Table I. Derivatives of Arylcyanomethylenequinone Oximes

Compound	M.P.[a] °C.	Yield %	Recrystallization Solvent	Analysis, %[b]
		Phenylisocyanate derivative of		
I	173–174	97	benzene	C,73.89; H,4.43; N,12.31 C,73.83; H,4.55; N,12.48
II	195	93	dioxane	C,67.11; H,3.76; N,11.18 C,66.95; H,3.63; N,11.30
III	160–161	92	benzene	C,71.15; H,4.62; N,11.31 C,71.32; H,4.84; N,11.36
IV	161–162	80	benzene	C,67.11; H,3.76; N,11.18 C,66.86; H,3.84; N,11.29
V	148–149	89	benzene-pet. ether[d]	C,71.15; H,4.62; N,11.31 C,71.02; H,4.68; N,11.44
VI	173–174	81	benzene	C,74.35; H,4.82; N,11.83 C,74.02; H,5.02; N,11.75
		1-Naphthylisocyanate derivative of		
I	169–170	95	benzene	C,76.71; H,4.38; N,10.74 C,76.40; H,4.51; N,10.75
II	192–193	92	benzene	C,70.53; H,3.78; N,9.86 C,70.53; H,3.93; N,9.60
III	168–170	99	benzene	C,74.10; H,4.54; N,9.97 C,74.19; H,4.64; N,10.04
IV	170–171	97	benzene	C,70.53; H,3.78; N,9.86 C,70.77; H,4.05; N,9.68
V	162	96	benzene	C,74.10; H,4.54; N,9.97 C,74.38; H,4.69; N,9.76
VI	161–163	93	benzene	C,76.77; H,4.72; N,10.62 C,76.67; H,4.77; N,10.82
		Acetyl derivative of		
I	145	62	CCl_4	C,72.66; H,4.59; N,10.60 C,72.69; H,4.70; N,10.71
II	185–186	57	CCl_4	C,64.32; H,3.72; N,9.38 C,64.25; H,3.75; N,9.52
III	131	89	CCl_4	C,69.38; H,4.79; N,9.52 C,69.67; H,4.94; N,9.85
IV	184	77	CCl_4	C,64.32; H,3.72; N,9.38 C,64.21; H,3.91; N,9.48
V	159–160	82	acetone	C,69.38; H,4.79; N,9.52 C,69.08; H,4.80; N,9.62
VI	133–136	57	CCl_4	C,73.36; H,5.07; N,10.07 C,73.17; H,5.06; N,10.10
		Benzoyl derivative of		
I	191–192	50	acetone	C,77.25; H,4.29; N,8.59 C,77.23; H,4.39; N,8.71
II	221–222	54	acetone	C,69.90; H,3.63; N,7.77 C,70.22; H,3.75; N,7.87
III	198–199	44	acetone	C,74.14; H,4.53; N,7.86 C,74.25; H,4.67; N,8.11
IV	196–198	53	acetone	C,69.90; H,3.63; N,7.77 C,69.78; H,3.69; N,7.94
V	175	56	acetone	C,74.14; H,4.53; N,7.86 C,73.90; H,4.50; N,7.94
VI	154–155	47	acetone	C,77.63; H,4.74; N,8.23 C,77.39; H,4.91; N,8.19
		p-Nitrobenzyl derivative of		
I	151	65	acetone	C,70.58; H,4.23; N,11.76 C,70.81; H,4.31; N,11.78
II	173–213	43	acetone	C,64.37; H,3.60; N,10.73 C,64.37; H,3.83; N,10.59
III	164–165	64	acetone	C,68.21; H,4.42; N,10.85 C,67.98; H,4.55; N,10.90
IV	200–201	82	acetone	C,64.37; H,3.60; N,10.73 C,64.46; H,3.83; N,10.77
V	162	72	benzene	C,68.21; H,4.42; N,10.85 C,68.04; H,4.58; N,11.01
VI	172–174	52	acetone	C,71.15; H,4.61; N,11.32 C,70.85; H,4.66; N,11.22

[a] All melting points are uncorrected. [b] Analyses by Midwest Microlab, Inc., Indianapolis, Ind. First series calculated, second found. [c] Melted with decomposition. [d] Petroleum ether, b.p. 60–71°. [e] A portion melted at 173°, the remainder at 213°. Probably a mixture of isomers.