After stirring for 14 hr, the solvent was removed from the reaction mixture, yielding a cream product which, after washing with CH_3OH, crystallized from EtOAc as cream needles, 0.23 g (36%), mp 185–187° (Table I).

Registry No.—6-Methyl-3-substituted 3*H*-isoxazolo[3,2-*c*]-[1,2,4]thiadiazoles, 55723-65-4 (R = 2,5-$Cl_2C_6H_3$), 55723-66-5 (R = 2-$NO_2C_6H_4$), 55723-67-6 (R = 3-$NO_2C_6H_4$), 55723-68-7 (R = 4-$NO_2C_6H_4$; 3-substituted 3*H*-thiazolo[2,3-*c*][1,2,4]thiadiazoles, 55723-69-8 (R = 3-$NO_2C_6H_4$), 55723-70-1 (R = 4-$NO_2C_6H_4$); 6-methyl-3-substituted 3*H*-1,3,4-thiadiazolo[2,3-*c*][1,2,4]thiadiazoles, 55723-71-2 (R = 2,5-$Cl_2C_6H_3$), 55723-72-3 (R = 3-$NO_2C_6H_4$), 55723-73-4 (R = 4-$NO_2C_6H_4$); 5-methyl-3-substituted 3*H*-thiadiazolo[4,3-*d*][1,2,4]thiadiazoles, 55723-74-5 (R = 2,5-$Cl_2C_6H_3$), 55723-75-6 (R = 3-$NO_2C_6H_4$); **1**, 1072-67-9; **2**, 55723-76-7; **3** (R = 5-CH_3-2-C_5H_3N; R_1 = 6-CH_3), 24097-95-8; **5** (X = O; Y = CPh; Z = N), 55723-77-8; **5** (X = S; Y = Z = CH), 55723-78-9; **5** (X = S; Y = CCH_3; Z = N), 55723-79-0; **5** (X = S; Y = N; Z = CCH_3), 55723-80-3; 2-amino-5-phenyl-1,3,4-oxadiazole, 1612-76-6; 2-aminothiazole, 96-50-4; 2-amino-5-methyl-1,3,4-thiadiazole, 108-33-8; 5-amino-3-methyl-1,2,4-thiadiazole, 17467-35-5; 2-amino-5-methylpyridine, 1603-41-4; trichloromethanesulfenyl chloride, 594-42-3.

References and Notes

(1) (a) Support of this work by U.S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged; (b) Eastman Kodak Fellow, 1974.

(2) For reviews on this topic see L. L. Bambas in "Five Membered Heterocyclic Compounds", Interscience, New York, N.Y., 1952, p 35; W. A. Shermann in "Heterocyclic Compounds", Vol. 7, R. C. Elderfield, Ed., Wiley, New York, N.Y., 1961, p 558; F. Kurzer, *Adv. Heterocycl. Chem.*, **5**, 119 (1965); F. Kurzer in "Organic Compounds of Sulfur, Selenium, and Tellurium", Vol. 1, D. H. Reid, Ed., The Chemical Society, London, 1970, p 446; F. Kurzer, *ibid.*, Vol. 2, 1973, p 721.

(3) J. Goerdeler and W. Roth, *Chem. Ber.*, **96**, 534 (1963); C. F. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. Van Allan, *J. Org. Chem.*, **24**, 779 (1959); H. Beecken, *Chem. Ber.*, **100**, 2159 (1967).

(4) (a) F. von Sturm and W. Hans, *Angew. Chem.*, **67**, 743 (1955); (b) K. Pilgram and R. D. Skiles, *J. Org. Chem.*, **38**, 1575 (1973).

(5) Von G. Barnikow and J. Bödeker, *J. Prakt. Chem.*, **313**, 1148 (1971); R. L. N. Harris, *Aust. J. Chem.*, **25**, 993 (1972).

(6) K. T. Potts and J. Kane, *J. Org. Chem.*, **38**, 3087 (1973); K. T. Potts and R. Armbruster, *ibid.*, **35**, 1965 (1970); **36**, 1846 (1971).

(7) H. Göth and H. Schmid, *Chimia*, **20**, 148 (1966); E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **88**, 1844 (1966); S. N. Ege, *J. Chem. Soc. C*, 2624 (1969); D. W. Kurtz and H. Shechter, *Chem. Commun.*, 689 (1966).

(8) K. T. Potts and J. Kane, unpublished results.

(9) S. McKenzie, B. B. Molloy, and D. H. Reid, *J. Chem. Soc. C*, 1908 (1966).

(10) Spectral characterizations were carried out on the following instrumentation: infrared spectra, Perkin-Elmer Model 337 spectrophotometer; ultraviolet spectra, Cary 14 spectrophotometer; NMR spectra, Varian T-60 and HA-100 spectrometers, using Me_4Si as an internal standard; mass spectra, Hitachi Perkin-Elmer RMU-6E mass spectrometer at 70 eV, utilizing the direct insertion probe technique with a source temperature of ca. 150°. All melting points were determined in capillaries using a Thomas-Hoover capillary melting point apparatus or a Mel-Temp apparatus. Evaporations were carried out under reduced pressure using a Buchi Rotovap apparatus. PLC was carried out on 20 × 20 mm plates using silica gel PF 254 with $CaSO_4$ (thickness and solvent as indicated). Microanalyses were by Galbraith Laboratories, Knoxville, Tenn., and Instranal Laboratory, Inc., Rensselaer, N.Y.

(11) Generally, partial decomposition of these sulfenamides during purification resulted in unsatisfactory analytical data.

(12) Alconox is the registered trade name of a phosphorus base wetting agent and detergent manufactured by Alconox Inc., New York, N.Y.

Reaction of 2-Arylhydrazono-3-oxonitriles with Hydroxylamine. Synthesis of 3-Amino-4-arylazoisoxazoles

Mohamed Hilmy Elnagdi,* Mohamed Rifaat Hamza Elmoghayar, Ebtisam Abdel Aziz Hafez, and Hikmat Hussein Alnima

Department of Chemistry, Faculty of Science, Cairo University, Giza, A.R., Egypt

Received February 27, 1975

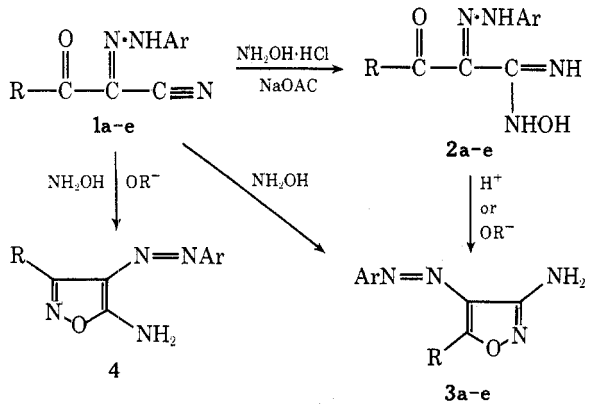
Whereas the 2-arylhydrazono-3-oxonitriles **1a–e** react with hydroxylamine hydrochloride and sodium acetate in refluxing ethanol to yield the amidoximes **2a–e**, 3-amino-4-arylazo 5-substituted isoxazoles (**3a–e**) are formed when **1a–e** are treated with hydroxylamine in aqueous ethanol. On the other hand, treatment of **1a–e** with hydroxylamine in the presence of excess methanolic sodium methoxide has resulted in the formation of the 5-amino-4-arylazo 3-substituted isoxazoles **4a–e**. Ethyl arylazocyanoacetate (**11a–e**) reacts with hydroxylamine hydrochloride and sodium acetate to yield the amidoximes **12a–e**, which could be readily cyclized into the 3-aminoisoxazoles **13a–e** by the action of methanolic sodium methoxide. The behavior of **2** toward the action of thionyl chloride, benzaldehyde, and hydrazines is reported.

Although several recent papers have dealt with the synthesis and biological evaluation of 4-arylazo-5-isoxazolones,[1-3] 4-arylazo-5-aminoisoxazoles have been neglected. We have now studied the reaction of some 2-arylhydrazono-3-oxonitriles with hydroxylamine as a source of aminoarylazoisoxazoles.

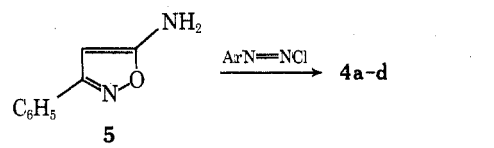
Treatment of the β-ketonitriles **1a–e** with NH_2OH·HCl and sodium acetate in refluxing ethanol led to amidoximes **2a–e**. Cyclization of these products with H_2SO_4 or sodium ethoxide gave the 3-aminoisoxazoles **3a–e**; these compounds were also obtained directly from the reaction of **1a–e** with NH_2OH in aqueous ethanol. The preferential attack of NH_2OH at the C≡N group in these reactions is in contrast to other findings,[4,5] which indicate that the CO group in **1a–e** is the more reactive electrophilic center in nonprotic media. The enhanced reactivity of the C≡N group in the hydroxylamine reactions is attributed to protonation. Consistent with this view are the findings that at pH 11, no reaction with NH_2OH occurred, and that in the presence of alkoxides, the 5-amino compounds **4a–e** were formed in good yield. Compounds **4a–d** were also obtained via action of aryldiazonium salts on 5-amino-3-phenylisoxazole (**5**). Although ethyl cyanoacetate derivatives have been shown to react with NH_2OH to yield either 3- or 5-aminoisoxazoles depending on reaction conditions,[6] 5-aminoisoxazoles or 5-isoxazolones are the only reported products from reaction of 3-oxonitriles with NH_2OH under a variety of acidic and basic conditions.[7-11]

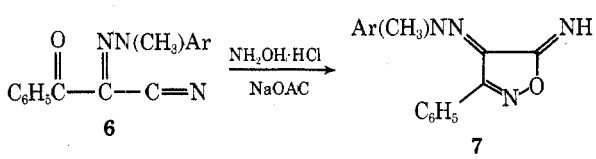
In contrast to the behavior of **1a–e**, the methylarylhydrazones **6a–d** reacted with NH_2OH·HCl and sodium acetate in refluxing ethanol to yield the 5-imino-2-isoxazolines **7a–d**. Compound **7a** was converted into 4-methylphenylhydrazono-3-phenyl-2-isoxazolin-5-one (**8**) by the action of ACOH–HCl mixture.

Similar to the behavior of **1a–e** toward the action of NH_2OH, the 2-phenylhydrazono-3-iminonitriles **9a,b**

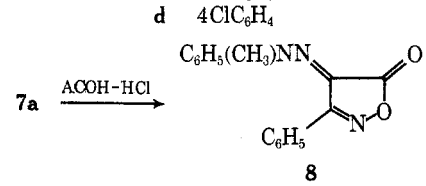


1-4 R Ar
a C_6H_5 C_6H_5
b C_6H_5 3-$CH_3C_6H_4$
c C_6H_5 4-$CH_3C_6H_4$
d C_6H_5 4-ClC_6H_4
e CH_3 C_6H_5

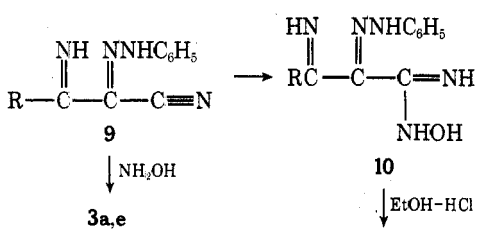




6, 7 Ar
a C_6H_5
b 3-$CH_3C_6H_4$
c 4-$CH_3C_6H_4$
d 4ClC_6H_4

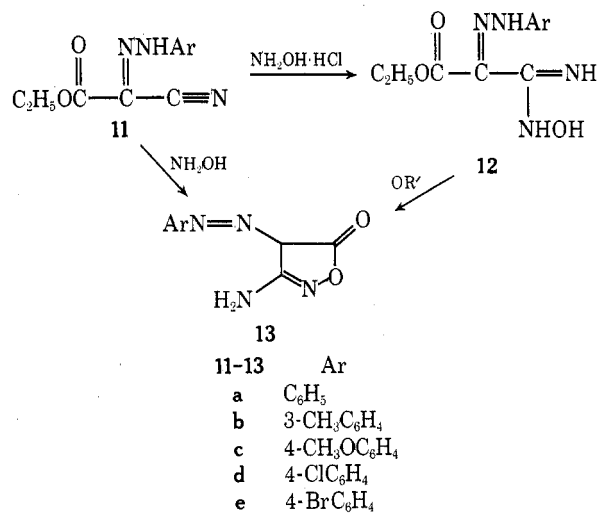


reacted with NH_2OH·HCl and sodium acetate to yield the amidoximes **10a,b.** The latter derivatives could be converted into **2a,e** by the action of ethanolic hydrochloric acid. On the other hand, **9a,b** reacted with NH_2OH in aqueous ethanol to yield compounds **3a,e.**



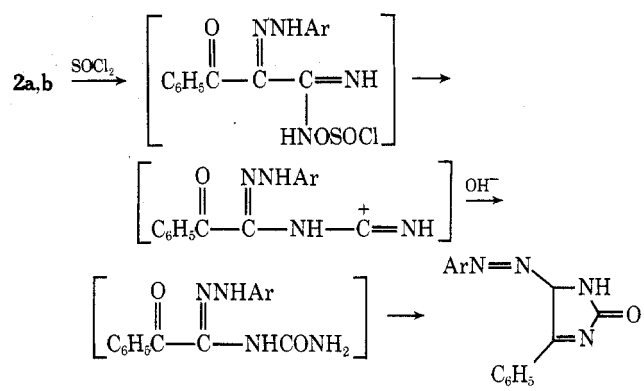
9, 10a, R = CH_3
b, R = C_6H_5

Conflicting results have been reported[12-14] for the reaction of ethyl arylazocyanoacetate (**11**) with hydroxylamine. As a part of the present investigation it was thought worthwhile to establish the behavior of **11a–e** toward NH_2OH. Thus, treatment of **11a–e** with NH_2OH·HCl and sodium acetates using the experimental procedure described by Bianchi[14] led to the formation of the amidoximes **12a–e** in good yields. Cyclization of **12a–e** by alkoxides afforded

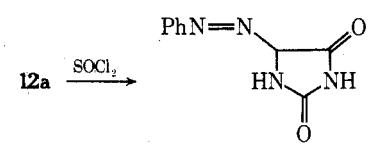


11-13 Ar
a C_6H_5
b 3-$CH_3C_6H_4$
c 4-$CH_3OC_6H_4$
d 4-ClC_6H_4
e 4-BrC_6H_4

13a–d. The latter compounds were obtained directly from reaction of **11a–e** with NH_2OH in aqueous ethanol. Treatment of **2a,b** with thionyl chloride, in benzene solution, resulted in their rearrangement into the 2-imidazolin-2-one derivatives **14a,b.** Similarly, the amidoxime **12a** rearranged into 4-phenylazohydantoin (**15**) by the action of the reagent.



14a, Ar = C_6H_5
b, Ar = 3-$CH_3C_6H_4$



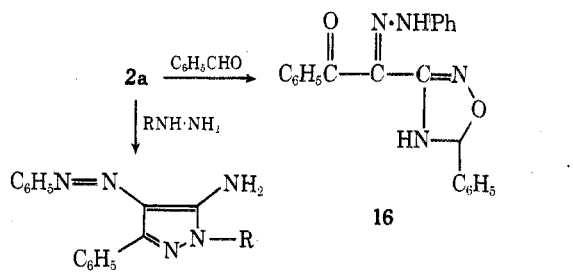
15

The formation of **14a,b** and **15** via rearrangement of **2a,b** and **12a** with thionyl chloride may be assumed to proceed by the rearrangement of the latter compounds into a urea derivative which then cyclizes into the corresponding imidazoline derivatives **14a,b** and **15.** This is similar to the reported Tiemann rearrangement of amidoximes with sulfonyl halides to give ureas.[15] An alternative to this mechanism may be the cyclization of the amidoximes **2a,b** and **12a** into the corresponding 2-aminoisoxazole derivative, which then rearranges into the final product via a mechanism similar to that considered recently by Nishiwaki et al.[16] for the rearrangement of 5-aminoisoxazoles into 3-imidazolin-2-ones. The latter possibility was however readily ruled out, since **3a,b** and **12a** were recovered almost unreacted when treated with thionyl chloride in benzene solution under the experimental conditions used to affect rearrangement of **2a,b** and **12a.**

When amidoximes are treated with aromatic aldehydes they are converted into 4,5-dihydro-1,2,4-oxadiazole deriv-

atives.[17] Thus, when **2a** was treated with benzaldehyde in the presence of piperidine, the 1,2,4-oxadizole derivative **16** was formed.

Compound **2a** reacted with hydrazine hydrate and with phenylhydrazine to yield the aminopyrazole derivatives **17a,b.**



16

17a, R = H
b, R = C_6H_5

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded (KBr) on a Perkin-Elmer Model 337 spectrophotometer. Satisfactory analytical data (±0.3% for C, H, N) were presented for all compounds in Tables I–IV.

Reaction of 1a–e, 9a,b, and 11a–e with Hydroxylamine Hydrochloride and Sodium Acetate. General Procedure. To a suspension of the compound (0.1 mol) in ethanol (100 ml) a solution of NH_2OH·HCl (0.1 mol) in 30 ml of water and 10 g of anhydrous sodium acetate were added. The reaction mixture was refluxed for 3 hr and then poured onto water. The solid product, so formed, was collected by filtration and crystallized from the proper solvent. The amidoxime derivatives **2a–e, 10a,b** and **12a–e** are listed in Table I.

Compounds **2a–e** showed ir bands at 1600–1610 (ν C=N), 1620–1625 (δ NH_2), 1630–1640 cm^{-1} (ν CO), 3265–3280 and 3340–3350 (ν NH_2), and 3470–3475 cm^{-1} (ν OH).

Compounds **10a,b** showed ir bands at 1625–1630 (ν C=N), 1640–1645 (δ NH_2), 3300 and 3400–3410 (ν NH_2), and 3450 cm^{-1} (ν OH).

Compounds **12a–e** showed ir bands at 1605–1610 (ν C=N), 1625–1640 (δ NH_2), 1690–1695 (ester CO), 3270–3275 and 3350–3355 (ν NH_2), and 3475–3480 cm^{-1} (ν OH).

3-Amino-4-arylazo 5-Substituted Isoxazoles (3a–e). A. From 1a–e or 9a,b and hydroxylamine. To a solution of the appropriate compound (0.1 mol) in ethanol (100 ml) was added an aqueous solution of NH_2OH (prepared by dissolving 0.1 mol of NH_2OH·HCl in 20 ml of water and neutralizing the resulting solution by addition of 0.1 equiv of Na_2CO_3). The reaction mixture was then refluxed for 4 hr, cooled, poured onto water, acidified with acetic acid, and left to stand. The solid product, so formed, was collected by filtration and crystallized from ethanol. The isoxazole derivatives **3a–e** are listed in Table II.

Compounds **3a–e** showed ir bands at 1616–1630 (δ NH_2), 3350–3365, and 3420–3450 cm^{-1} (ν NH_2).

B. From 2a–e and Concentrated Sulfuric Acid. Concentrated sulfuric acid (2 ml, 98%) was added to each of **2a–e** (3 g). The reaction mixture was kept at room temperature for 2 hr and then poured onto ice-cold water. The solid product, so formed, was collected by filtration, crystallized from ethanol, and identified (melting point, mixture melting point, and ir) as **3a–e.**

C. From 2a–e and Methanolic Sodium Methoxide. To a sodium methoxide solution (prepared from 1.0 g of sodium metal and 80 ml of methanol), 5 g of each of **12a–e** was added. The reaction mixture was then refluxed for 1 hr, left to cool, poured over water, and acidified with concentrated hydrochloric acid. The solid product, so formed, was collected by filtration and identified (melting point and mixture melting point) as **3a–e.**

Reaction of 1a–e with Hydroxylamine at pH 11. Compounds **1a–e** were recovered almost unaffected after being refluxed with an equivalent amount of NH_2OH in ethanolic solution the pH of which was adjusted to 11.

5-Amino 3-Substituted 4-Arylazoisoxazoles (4a–e). A. From 1a–e and Hydroxylamine. To a suspension of each of **1a–e** (0.1 mol) in ethanol (50 ml), hydroxylamine hydrochloride (0.1 mol) and methanolic sodium methoxide (prepared from 5 g of sodium metal and 100 ml of ethanol) were added. The reaction mixture was refluxed for 12 hr and then evaporated in vacuo. The remaining solid product was dissolved in water and neutralized by addition of acetic acid. The resulting solid product was collected by filtration and crystallized from ethanol. The isoxazole derivatives **4a–e,** listed in Table III, were further purified by crystallization from ethanol.

Compounds **4a–e** showed ir bands at 1615–1620 (δ NH_2) and 3330–3340 and 3420–3430 cm^{-1} (ν NH_2).

B. From 5-Amino-3-phenylisoxazole and Aryldiazonium Salts. A solution of **5** (14.6 g) in acetic acid (100 ml) was treated with a solution of 5 g of anhydrous sodium acetate in 35 ml of water and then with the appropriate aryldiazonium salt (prepared from 0.1 mol of the amine and the corresponding quantity of sodium nitrite). The reaction mixture was left at room temperature for 1 hr and the solid product, so formed, was collected by filtration, crystallized, and identified (melting point and mixture melting point) as **4a–e.**

5-Ketimino-4-methylarylhydrazono-3-phenyl-2-isoxazolines (7a–d). Each of **6a–d** was treated with NH_2OH·HCl and anhydrous sodium acetate using the same experimental procedure previously described for the reaction of **1a–e** with the same reagents. The resulting reaction solution was poured onto water and the resulting solid products were collected by filtration and crystallized from ethanol. The 5-imino-2-isoxazoline derivatives **7a–d** are listed in Table IV.

Compounds **7a–d** showed ir bands at 1610–1620 (ν C=N) and 3400–3410 cm^{-1} (ν NH).

4-Methylphenylhydrazono-3-phenyl-2-isoxazolin-5-one (8). A suspension of **7a** (5 g) in acetic acid (90 ml) and hydrochloric acid (10 ml, 30%) was refluxed for 1 hr and then evaporated in vacuo. The remaining solid product was identified (melting point and mixture melting point) as the known 8.[18]

Hydrolysis of 10a,b with Ethanolic Hydrochloric Acid. To a suspension of each of **10a,b** (5 g) in ethanol (80 ml) was added 20 ml of hydrochloric acid (30%). The reaction mixture was refluxed for 10 min and then left to cool. The solid product, so formed, was

Table I
List of the Amidoxime Derivatives 2a–e, 10a, b, and 12a–e

Compd	Yield, %	Crystn solvent[a]	Mp, °C	Formula
2a	90	a	156	$C_{15}H_{14}O_2N_4$
2b	95	a	165	$C_{16}H_{16}O_2N_4$
2c	85	a	169	$C_{16}H_{16}O_2N_4$
2d	80	a	166	$C_{15}H_{13}O_2N_4Cl$
2e	85	b	180	$C_{10}H_{12}O_2N_4$
10a	78	c	191	$C_{10}H_{13}ON_5$
10b	75	c	126	$C_{15}H_{15}ON_5$
12a	70	d	198	$C_{11}H_{14}O_3N_4$
12b	82	d	200	$C_{12}H_{16}O_3N_4$
12c	85	d	222	$C_{12}H_{16}O_4N_4$
12d	80	c	192	$C_{11}H_{13}O_3N_4Cl$
12e	80	c	200	$C_{11}H_{13}O_3N_4Br$

[a] a, ethanol; b, dioxane; c, 2-propanol; d, dioxane–2-propanol (1:1).

Table II
List of 4-Arylazo-3-amino 5-Substituted Isoxazoles 3a–e and 13a–e

Compd	Yield, %	Mp, °C	Formula
3a	90	186	$C_{15}H_{12}ON_4$
3b	92	150	$C_{16}H_{14}ON_4$
3c	95	194	$C_{16}H_{14}ON_4$
3d	89	225	$C_{15}H_{11}ON_4Cl$
3e	89	171	$C_{10}H_{10}ON_4$
13a	80	208	$C_9H_8O_2N_4$
13b	85	245	$C_{10}H_{10}O_2N_4$
13c	85	228	$C_{10}H_{10}O_3N_4$
13d	80	210	$C_9H_7O_2N_4Cl$
13e	90	260	$C_9H_7O_2N_4Br$

Table III
List of 5-Amino-4-arylazo 3-Substituted Isoxazole Derivatives (4a–e)

Compd	Yield, %	Mp, °C	Formula
4a	60	141	$C_{15}H_{12}ON_4$
4b	65	151	$C_{16}H_{14}ON_4$
4c	58	144	$C_{16}H_{14}ON_4$
4d	57	172	$C_{15}H_{11}ON_4Cl$
4e	50	166	$C_{10}H_{10}ON_4$

Table IV
List of 5-Ketimino-4-methylarylhydrazono-3-phenyl-2-isoxazolines (7a–d)

Compd	Yield, %	Mp, °C	Formula
7a	68	136	$C_{16}H_{14}ON_4$
7b	70	164	$C_{17}H_{16}ON_4$
7c	70	198	$C_{17}H_{16}ON_4$
7d	67	154	$C_{16}H_{13}ON_4Cl$

collected by filtration and identified (melting point and mixture melting point) as **2a** and **2e**, respectively.

3-Amino-4-arylazo-2-isoxazolin-5-ones (13a–e). A. From 11a–e and Hydroxylamine. The experimental conditions described previously for the synthesis of **3a–e** from **1a–e** and hydroxylamine were adopted. The reaction products **13a–e** are listed in Table II.

Compounds **13a–e** showed ir bands at 1625–1635 (δ NH_2), 1690–1695 (CO), and 3350–3360 and 3415–3420 cm^{-1} (ν NH_2).

B. From 12a–e and Methanolic Sodium Methoxide. The experimental conditions previously used to effect cyclization of **2a–e** into **3a–e** by the action of sodium methoxide were adopted and the reaction products were identified (melting point and mixture melting point) as **13a–e.**

4-Arylazo-3-imidazolin-2-one (14a,b). To a solution of each of **2a,b** (5 g) in dry benzene (100 ml), thionyl chloride (10 ml) was added. The reaction mixture was kept for 2 hr at room temperature and then poured onto ice-cooled water. The benzene layer was then separated, dried, and evaporated. The resulting solid products, **14a,b,** were crystallized from ethanol.

14a: red crystals, mp 200°, ir 1615 (C=N), 1680 (C=O), and 3430 cm^{-1} (NH).

Anal. Calcd for $C_{16}H_{14}ON_4$: C, 69.05; H, 5.07; N, 20.13. Found: C, 68.97; H, 5.00; N, 20.20.

4-Phenylazohydantoin (15). Compound **12a** was treated with benzene and thionyl chloride using the same experimental procedure previously adopted for synthesis of **14a,b** from **2a,b.** The reaction product was purified by crystallization from acetic acid and identified (melting point, mixture melting point, and ir) as the known **15.**[19]

Reactions of 2a. A. With Benzaldehyde. To a mixture of **2a** (2 g) and benzaldehyde (1 ml) 1 drop of piperidine was added. The reaction mixture was heated at 100° (bath temperature) for 4 hr, then triturated with ethanol and left to stand. The crystals that separated were collected by filtration and recrystallized from ethanol to yield 1.5 g of **16:** mp 100°; ir 1660 (CO) and 3340 and 3420 cm^{-1} (ν NH groups).

Anal. Calcd for $C_{22}H_{18}O_2N_4$: C, 71.33; H, 4.90; N, 15.13. Found: C, 71.50; H, 4.61; N, 15.00.

B. With Hydrazines. A mixture of **2a** (2 g) and hydrazine hydrate (1 ml, 98%) or phenylhydrazine (1.5 ml) was heated at 100° (bath temperature) for 3 hr. The reaction mixture was then treated with dilute hydrochloric acid to remove the excess hydrazine and the resulting solid product was collected by filtration, crystallized, and identified (melting point and mixture melting point) as **16a** in case of **2a** and hydrazine hydrate and **16b** in case of **2a** and phenylhydrazine.

Registry No.—**1a,** 13491-70-8; **1b,** 40257-77-0; **1c,** 22744-14-5; **1d,** 22744-17-8; **1e,** 28317-57-9; **2a,** 55621-95-9; **2b,** 55621-96-0; **2c,** 55621-97-1; **2d,** 55621-98-2; **2e,** 55621-99-3; **3a,** 55622-00-9; **3b,** 55622-01-0; **3c,** 55622-02-1; **3d,** 55622-03-2; **3e,** 55622-04-3; **4a,** 55622-05-4; **4b,** 55622-06-5; **4c,** 55622-07-6; **4d,** 55622-08-7; **4e,** 55622-09-8; **5,** 4369-55-5; **6a,** 54670-89-2; **6b,** 54670-91-6; **6c,** 54670-92-7; **6d,** 54670-93-8; **7a,** 55622-12-1; **7b,** 55622-11-2; **7c,** 55622-12-3; **7d,** 55622-13-4; **9a,** 5110-91-8; **9b,** 15590-17-7; **10a,** 55622-14-5; **10b,** 55622-15-6; **11a,** 5335-36-4; **11b,** 3994-20-5; **11c,** 51337-35-0; **11d,** 3994-24-9; **11e,** 3994-25-0; **12a,** 55622-16-7; **12b,** 55622-17-8; **12c,** 24793-33-7; **12d,** 55622-18-9; **12e,** 55622-19-0; **13a,** 55622-20-3; **13b,** 55622-21-4; **13c,** 55622-22-5; **13d,** 55622-23-6; **13e,** 55622-24-7; **14a,** 55622-25-8; **14b,** 55622-26-9; **16,** 55622-27-0; hydroxylamine hydrochloride, 5470-11-1; benzaldehyde, 100-52-7; benzenediazonium chloride, 100-34-5; 3-methylbenzenediazonium chloride, 2028-72-0; 4-methylbenzenediazonium chloride, 2028-84-4; 4-chlorobenzenediazonium chloride, 2028-74-2.

References and Notes

(1) L. A. Summers, British Patent 1,080,864 (1967); *Chem. Abstr.*, **68,** 87286y (1968).
(2) P. F. H. Freeman, J. M. Pedlar, and I. T. Kay, German Patent 2,024,393 (1970); *Chem. Abstr.*, **74,** 53830e (1971).
(3) H. G. Garg and P. P. Singh, *J. Med. Chem.*, **13,** 1250 (1970).
(4) M. H. Elnagdi, N. A. L. Kassab, M. E. E. Sobhy, M. R. Hamza, and M. U. Wahby, *J. Prakt. Chem.*, **314,** 815 (1972).
(5) M. H. Elnagdi, M. R. H. Elmoghayar, and D. H. Fleta, *J. Prakt. Chem.*, **316,** 975 (1974).
(6) L. Bauer and C. N. V. Nabury, *J. Org. Chem.*, **26,** 4917 (1961).
(7) A. Obregia, *Justus Liebigs Ann. Chem.*, **266,** 329 (1891).
(8) H. M. Wuest and M. Hoffer, U.S. Patent 2,430,094 (1947); *Chem. Abstr.* **42,** 1610 (1948).
(9) S. Yamada and C. Kowaki, *J. Pharm. Soc. Jpn.*, **71,** 1356 (1951).
(10) S. Yamada and C. Yukiwaki, Japanese Patent 4726 (1952); *Chem. Abstr.*, **47,** 11255 (1953).
(11) S. Cusmano, V. Sprio, and F. Traponi, *Gazz. Chim. Ital.*, **82,** 98 (1952).
(12) C. Bertini, *Gazz. Chim. Ital.*, **31,** 578 (1901).
(13) R. C. Dubenko and P. S. Pel'Kis, Russian Patent 161,762 (1964); *Chem. Abstr.*, **61,** 3115 (1965).
(14) M. Bianchi, A. Buttl, and S. Rossi, *Tetrahedron*, **30,** 2765 (1974).
(15) D. V. Banthorpe in "The Chemistry of the Amino Group", S. Patai, Ed., Interscience, New York, N.Y., 1968, p 628.
(16) T. Nishiwaki and T. Saito, *J. Chem. Soc. C*, 2648 (1971).
(17) J. Hirro and Y. Kato, *Bull. Chem. Soc. Jpn.*, **45,** 2055 (1972).
(18) A. Mustafa, W. Asker, A. H. Harhash, and A. M. Fleifel, *Tetrahedron*, **21,** 2215 (1965).
(19) S. N. Baranov and T. V. Perova, *Khim. Geterotsikl. Soedin.*, **2,** 326 (1967); *Chem. Abstr.*, **68,** 2855k (1968).