

## CYANOACETARYLAMIDES—I

### PREPARATION AND REACTIONS OF THEIR ARYLAZO DERIVATIVES WITH DIAZONIUM ION AND GRIGNARD REAGENTS

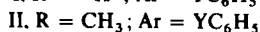
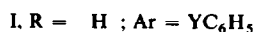
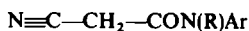
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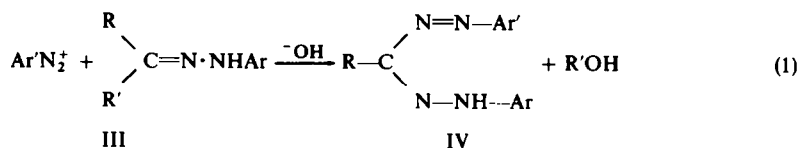
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**Abstract**—The preparation and spectral properties of twenty-five arylazocycanoacetaryl amides (VI–VIII) are investigated. Analysis of the IR and UV spectra of such compounds (VI–VIII) shows that they are of the hydrazo rather than the azo form. The reaction of benzenediazonium ion and the arylazo derivatives (VI and VII) in the presence of sodium hydroxide (and not in the presence of sodium acetate) produces 3-cyano-1,5-diarylformazans (IX). A mechanism is suggested for the formation of formazans (IX). Reaction of (VI–VII) with Grignard reagents results in 1,2-addition to the cyanide group with the formation of arylazoiminoacylacetanilides (X), which were hydrolysed to the corresponding arylazoacylacetanilides (XI). The UV spectral properties of compounds X and XI are compared.

THE COUPLING of diazonium salts to a  $\text{CH}_2$  group activated by a cyano and some other group is a well known reaction.<sup>1</sup> An examination of the nitriles that have been subjected to this reaction reveals that the cyanoacetaryl amides (I–II) have received little, if any, attention. Furthermore, diazonium ions are known to react with aliphatic



azo compounds of type III with displacement of hydrogen, acetyl, carboxyl and ethoxycarbonyl groups and the formation of formazans (IV) (reaction 1). The simultaneous coupling and cleavage of the  $\text{R}'$  group resembles the Japp-Klingemann type



of reaction from which many monoazo intermediates have been isolated.<sup>2</sup> The cleavage of the phenylcarbonyl group in such arylazo derivatives (III;  $\text{R}' = \text{CONH C}_6\text{H}_5$ ) by diazonium ion has not been reported before.

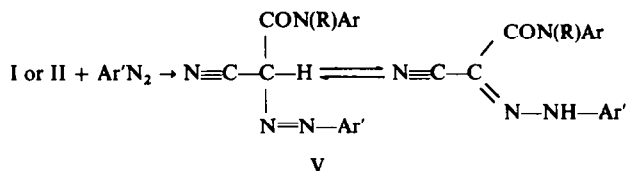
The present investigation deals with the preparation of a series of arylazocycanoacetaryl amides (VI–IX) and their behaviour towards further coupling with diazonium ions. Also, the reactions of such arylazocycanoacetaryl amides with Grignard reagents have been studied.

## RESULTS AND DISCUSSION

*Synthesis and structure of arylazocynoacetaryl amides*

In a NaOAc buffered solution of EtOH, cyanoacetaryl amides (I-II) react with diazotized arylamines to yield arylazocynoacetaryl amides (VI-VIII) in 60-80% (Scheme 1).

SCHEME 1



VI, R = H; Ar = C<sub>6</sub>H<sub>5</sub>; Ar' = R'C<sub>6</sub>H<sub>4</sub>

VII, R = H; Ar = R'C<sub>6</sub>H<sub>4</sub>; Ar' = C<sub>6</sub>H<sub>5</sub>

VIII, R = CH<sub>3</sub>; Ar = Ar' = C<sub>6</sub>H<sub>5</sub>

- |                             |                             |   |
|-----------------------------|-----------------------------|---|
| a, R' = H                   | g, R' = 2-CH <sub>3</sub> O | m, R' = 4-NO <sub>2</sub>                   |
| b, R' = 4-CH <sub>3</sub>   | h, R' = 4-Cl                | n, R' = 3-NO <sub>2</sub>                   |
| c, R' = 3-CH <sub>3</sub>   | i, R' = 3-Cl                | o, R' = 2-HO                                |
| d, R' = 2-CH <sub>3</sub>   | j, R' = 2-Cl                | p, R' = 2-HO <sub>2</sub> C                 |
| e, R' = 4-CH <sub>3</sub> O | k, R' = 4-Br                | q, R' = 4-(CH <sub>3</sub> ) <sub>2</sub> N |
| f, R' = 3-CH <sub>3</sub> O | l, R' = 3-Br                |   |

IR spectra of the compounds (VI-VII) indicate that they are hydrazones rather than azo compounds. For example, phenylazocynoacet-N-methylanilide (VIII), exhibits an NH stretching band near 3247 cm<sup>-1</sup>. The hydrazone structure (VIII) but not the azo structure (V) requires an NH group to be present. All other compounds (VI-VIII) exhibited two bands between 3100 and 3400 cm<sup>-1</sup> in the solid state.

Further, the IR spectra of the starting anilides (I-II), like other saturated alkyl nitriles,<sup>3</sup> showed C≡N stretching bands near 2260 cm<sup>-1</sup>. On the other hand, their arylazo derivatives (VI-VIII) exhibit their C≡N absorption at 2220 cm<sup>-1</sup>. That these bands are about 40 cm<sup>-1</sup> lower in frequency than those of both the corresponding anilides (I-II) and the saturated nitriles substantiates the presumed hydrazone structure in which the C≡N group is in conjunction with a C=N double bond. α,β-Unsaturated nitriles are known to absorb in the 2235-2215 cm<sup>-1</sup>.<sup>3</sup>

In addition, the IR data of the azo compounds (VI-VIII) reveal that their amide CO stretching vibrations are at lower frequencies than those of the corresponding cyanoacetaryl amides (I-II). Such a shift excludes the possibility of an azo structure which requires the amide CO stretch of both the anilide and its azo derivative to be almost the same. The observed down shift of the amide CO stretch of the compounds (VI-VIII) can be rationalized in terms of conjugation with the C=N double bond and possible chelation effects as required by the hydrazone structure. Conjugation of the CO group with either C=C or C=N is reported<sup>4,5</sup> to cause the CO stretch to fall by 20 to 30 cm<sup>-1</sup>. Typical spectral data are recorded in Table 1.

The electronic absorption spectra (Table 2) provide additional evidence that the coupling products (VI-VIII) are of the hydrazone rather than the azo form. It has been reported<sup>2c</sup> that the UV spectra of monophenylazo compounds differ from those of

TABLE 1. CHARACTERISTICS IR ABSORPTION BANDS OF TYPICAL ARYLAZOCYANOACETARYLAMIDES

Compound No.	$\nu\text{N—H}$ $\text{cm}^{-1}$	$\nu\text{C}\equiv\text{N}$ $\text{cm}^{-1}$	$\nu\text{C=O}$ $\text{cm}^{-1}$	$\nu\text{C=N}$ $\text{cm}^{-1}$	$\nu\text{C—N—H}$ $\text{cm}^{-1}$
VIa	3310, 3225*	2220*	1660*	1565*	1536*
VIb	3333, 3226, 3185	2222	1653	1550	1538
VIc	3330, 3225*	2222*	1660*	1560*	1535*
VId	3333, 3226	2222	1661	1563	1538
VIe	3333, 3175	2222	1667	1563	1531
VIh	3300, 3226	2227	1658	1563	1538
VIi	3279, 3247	2222	1661	1563	1538
VIIm	3333, 3226	2227	1667	1563	1538
VIIn	3367, 3175	2222	1663	1563	1538
VIII	3247	2222	1626	1563	

\* Determined in KBr disks

TABLE 2. UV SPECTRA OF ARYLAZO CYANOACETARYLAMIDES

Compound No.	$\lambda_{\text{max}}^{\text{MeOH}}, \text{m}\mu (\log \epsilon)$		
VIa	360 (4.34)	280 (3.75)	235 (4.35)
VIb	369 (4.33)	290 (3.72)	239 (4.32)
VIc	363 (4.33)		237 (4.31)
VId	364 (4.31)		236 (4.25)
VIe	380 (4.34)	299 (3.87)	239 (4.33)
VIc	364 (4.33)	264 (3.84)	234 (4.18)
VIg	380 (4.35)		235 (4.30)
VIh	363 (4.33)	295 (3.92)	236 (4.34)
VIi	358 (4.32)	288 (3.86)	236 (4.34)
VIj	358 (4.36)		232 (4.29)
VIk	365 (4.38)	297 (3.94)	236 (4.36)
VIl	358 (4.37)		236 (4.37)
VIIm	374 (4.50)		232 (4.32)
VIIn	348 (4.35)	266 (4.14)	231 (4.43)
VIo	381 (4.36)		236 (4.30)
VIp	368 (4.37)		233 (4.32)
VIb	362 (4.33)		238 (4.37)
VIc	363 (4.26)		238 (4.27)
VIe	365 (4.23)		239 (4.26)
VIIf	360 (4.30)		237 (4.26)
VIh	364 (4.35)	283 (3.80)	240 (4.40)
VIi	360 (4.34)	283 (3.79)	239 (4.34)
VIIm	367 (4.43)		
VIIn	360 (4.32)	270 (4.04)	239 (4.39)
VIII	354 (4.32)		235 (4.14)

monophenylhydrazones. The azo compounds have a strong K-band at 270–280  $\text{m}\mu$ . The monophenylhydrazones give a weak absorption band (or no band) at 284–295  $\text{m}\mu$  and a strong band at a wavelength higher than 320  $\text{m}\mu$ . The UV spectra of the compounds (VI–VIII) are similar to those of the typical hydrazones.

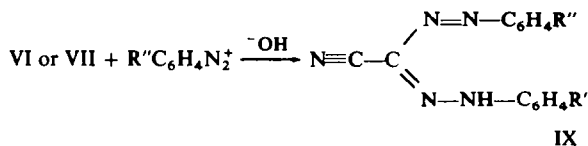
*Displacement of Arylcarbamoyl group by Diazonium ion*

When benzenediazonium chloride solution was added to phenylazocyanacetanilide (VIa) in NaOAc buffered EtOH, the phenylazo compound (VIa) was recovered. On the other hand, when the coupling of benzenediazonium ion to VIa was carried out in presence of NaOH, a reddish orange product was obtained, m.p. 160–161° and analysed as C<sub>14</sub>H<sub>11</sub>N<sub>5</sub>. IR spectrum (in nujol) showed the absence of the amide CO band observed in the IR spectrum of VIa. Its electronic absorption spectrum (MeOH) is analogous to that of a typical formazan.<sup>6</sup> It exhibited three maxima at 424 (log ε = 4.36), 288 (log ε = 4.17) and 261 (log ε = 4.08) mμ. Such a spectrum is quite different from that of the starting phenylazocyanacetanilide (VIa). That product was finally recognized as 3-cyano-1,5-diphenylformazan (IXa). A mixed melting point with an authentic sample of 3-cyano-1,5-diphenylformazan prepared by coupling of two equivalents of benzenediazonium ion to one equivalent to cyanoacetic acid according a method previously described,<sup>7</sup> showed no depression. This result suggests that the phenylcarbamoyl group underwent hydrolytic cleavage during coupling.

That the arylcarbamoyl group is, in fact, cleaved during azo coupling of VIa was further confirmed by the following: (i) compound IXa was the only product obtained from the coupling of benzenediazonium chloride with phenylazo derivatives of either cyanoacet-*p*-toluidide (VIIb), cyanoacet-*p*-chloroanilide (VIIh) or cyanoacet-*m*-nitroanilide (VIIn), (ii) 3-cyano-1-phenyl-5-*p*-bromophenylformazan (IXk) has been obtained from the reaction of benzenediazonium chloride with *p*-bromophenylazocyanacetanilide (VIk) and also from the reaction of *p*-bromobenzenediazonium chloride with phenylazocyanacetanilide (VIa), and (iii) 3-cyano-1-phenyl-5-*p*-methoxyphenylformazan (IXg) was similarly prepared from the corresponding azocyanacetanilides.

Similarly, the coupling of other arylazoderivatives of cyanoacetanilide (VI) with various diazotized arylamines was found to yield the corresponding 3-cyano-1,5-diarylformazans in 60–70%. (Scheme 2). All formazans (IXa–k) are new with the exception of IXa–d, which were synthesized by different methods.<sup>7</sup>

SCHEME 2



- |  |  |
|--|--|
| a. R' = R'' = H                        | g. R' = H; R'' = 4-CH <sub>3</sub> O               |
| b. R' = R'' = 4-NO <sub>2</sub>        | h. R' = R'' = 4-CH <sub>3</sub> O                  |
| c. R' = R'' = 2-HO <sub>2</sub> C      | i. R' = CH <sub>3</sub> O; R'' = 4-NO <sub>2</sub> |
| d. R' = R'' = 4-NO <sub>2</sub>        | j. R' = 4-CH <sub>3</sub> O; R'' = 4-Br            |
| e. R' = H; R'' = 4-NO <sub>2</sub>     | k. R' = H; R'' = 4-Br                              |
| f. R' = 4-NO <sub>2</sub> ; R'' = 4-Br |  |

The formazans (IXa–k) are intensely colored; they all exhibit absorption bands above 400 mμ. Their electronic absorption spectral data are recorded in Table 3.

The cleavage of the arylcarbamoyl group and the formation of formazan during the coupling of diazonium ion to VI–VII can be accounted for by one of the two

mechanistic paths shown in Scheme 3. The fact that the coupling of diazonium ion to arylazo cyanoacetarylamides occurs only in the presence of NaOH and not NaOAc supports that the reaction proceeds most rapidly with the anion (A-B) of the hydrazone (V). The diazonium ion may attack such an anion either at the nitrogen forming a tetrazene intermediate (C) or at the methine carbon giving bis-arylazo intermediate (D). Analogous intermediates were postulated for the coupling of benzenediazonium ion with aldehyde arylhydrazones<sup>8</sup> and with 1,3-diphenyl-1,2,3-propane-trione-2-phenylhydrazones.<sup>2c</sup> The tetrazene intermediates are known to be unstable and readily rearrange at room temperature.<sup>12</sup>

#### Reactions of arylazoacetarylamides with Grignard reagents

$\alpha,\beta$ -Unsaturated nitriles are known<sup>9</sup> to undergo 1,4-addition of Grignard reagent to the conjugated system. Since the compounds (VI-VII) in this study have the grouping  $N\equiv C-C=N-$ , which is analogous to  $N\equiv C-C=C-$  group, we felt it interesting to investigate the reactions of VIa and VIb, as typical examples of the series studied, with Grignard reagents to see whether they undergo the normal 1,2-addition or the 1,4-addition.

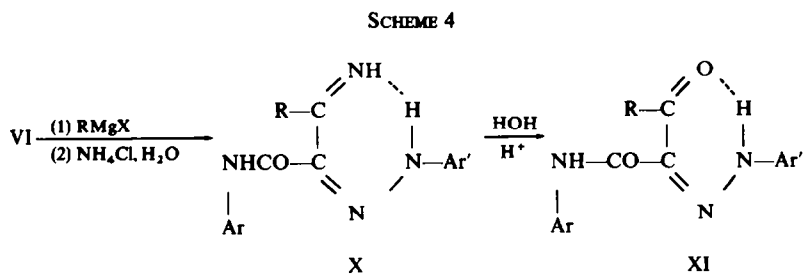
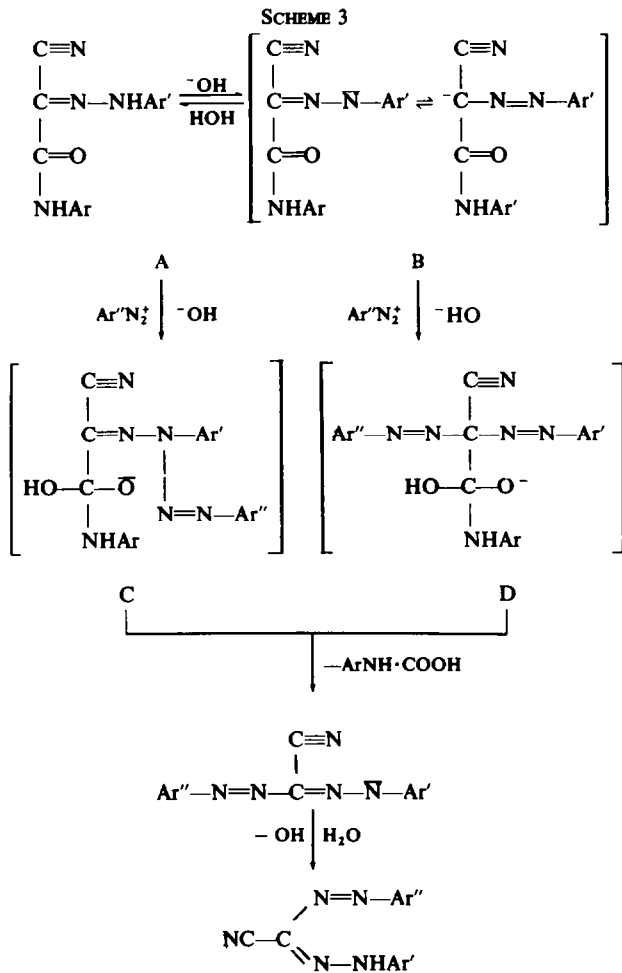
TABLE 3. ELECTRONIC ABSORPTION SPECTRA OF 3-CYANO-1,5-DIARYLFORMAZANS

Compound No.	$\lambda_{\max}^{\text{MeOH}}$ m $\mu$ .	(log $\epsilon$ )
IXa	424 (4.34)	288 (4.11) 261 (4.08)
IXb	453 (4.43)	291 (4.09) 264 (4.06)
IXc	366 (4.29)	227 (4.31)
IXd	377 (4.50)	223 (4.28)
IXe	425 (4.44)	299 (4.04) 225 (4.03)
IXf	429 (4.47)	305 (4.05) 246 (3.99)
IXg	445 (4.38)	296 (4.02) 260 (4.11)
IXh	470 (4.26)	268 (3.97)
IXi	441 (4.59)	334 (4.13) 245 (4.09)
IXj	444 (4.03)	290 (4.13) 266 (4.12)
IXk	441 (4.33)	289 (4.06) 263 (4.02)

When VIa was treated with an excess of PhMgBr 1,2-addition of one mole of the Grignard reagent to the nitrile group took place with the formation of Xa. Similarly, VIb reacted with one equivalent of the same reagent to give Xb. Treatment of VIa with MeMgI or EtMgBr gave Xc or Xd, respectively (Scheme 4).

The products Xa-d were identified by elemental and spectral analyses, or by their conversion to known compounds. For example, when Xa-c were refluxed in 10 M HCl the corresponding arylazoacylacetanilides XIa-c were formed. M.m.ps of each of XIa-c with an authentic sample, prepared by coupling the corresponding acylacetanilide with the appropriate arenediazonium chloride as previously described,<sup>5</sup> showed no depression. Hydrolysis of Xd under similar conditions gave phenylazopropionylacetanilide (XIId).

Analysis of the electronic absorption spectra (Fig. 1) of the compounds Xa-d in MeOH indicates that each compound has three absorption bands in the 200-400 m $\mu$ . These are referred to as A, B and C bands starting from the longer wavelength side. The data are recorded in Table 4. Such absorption patterns are analogous to those of



- a. R = Ar = Ar' = C<sub>6</sub>H<sub>5</sub>  
 b. R = Ar = C<sub>6</sub>H<sub>5</sub>; Ar' = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
 c. R = CH<sub>3</sub>; Ar = Ar' = C<sub>6</sub>H<sub>5</sub>  
 d. R = CH<sub>3</sub>-CH<sub>2</sub>; Ar = Ar' = C<sub>6</sub>H<sub>5</sub>

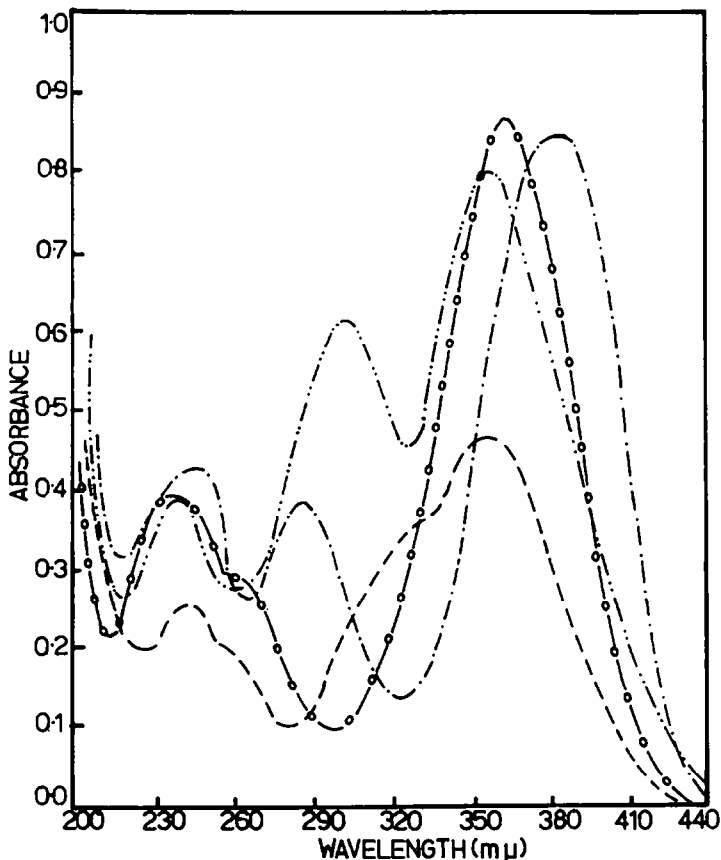


FIG. 1. Electronic absorption spectra of: *p*-tolylazobenzoylacetanilide (— · — · —); *p*-tolylazoiminobenzoylacetanilide (—); phenylazopropionylacetanilide (—○—○—); and phenylazoiminopropionylacetanilide (— — — —) in MeOH

the corresponding arylazo derivatives of acylacetanilides (XIa-d) (Fig. 1). Therefore, it would not be unreasonable to conclude that compounds (Xa-d), by analogy to compounds (XIa-d), have the hydrazone structure indicated (Scheme 4). We had previously shown that compounds of the type XI are arylhydrazones rather than azo compounds.<sup>5, 10</sup>

A comparison of  $\lambda_{\text{max}}$  of band A between any pair of compounds showed a significant amount of red shift for the acyl derivative (XI) over the iminoacyl compound (X) (Table 4). Such a bathochromic shift might be considered to be due to the difference in polarity between the C=O and C=NH groups. It was pointed out<sup>11</sup> that the K-band for chromophore A(CH=CH)<sub>n</sub>B is displaced to longer wavelengths as the electron attracting power of the terminal group B increases. In general, the group C=S at the end of such a system is more effective than C=O, which in turn, is much more effective than C=NH and C=CH<sub>2</sub>. In addition, being less electronegative, the imino nitrogen of the C=NH group will be less effective as the oxygen atom of the C=O group in stabilizing chelate rings (as in X and XI), a factor which is known to stabilize the excited state and decreases the energy of the electronic transition.<sup>10</sup>

TABLE 4. UV SPECTRA OF ARYLAZO DERIVATIVES OF ACYL AND IMINOACYL-ACETANILIDE

Compound No.		$\lambda_{\text{max}}^{\text{MeOH}}$ , m $\mu$ (log $\epsilon$ )	
Xa	360 (4.41)	320 (4.41)	245 (4.20)
XIa	376 (4.45)	284 (4.19)	245 (4.21)
Xb	360 (4.32)	320 (4.17)	245 (4.12)
XIb	385 (4.49)	286 (4.19)	248 (4.21)
Xc	360 (4.34)	305 (4.07)	238 (4.21)
XIc	368 (4.40)	266 (3.90)	236 (4.13)
Xd	362 (4.40)	305 (4.34)	242 (4.09)
XId	368 (4.47)	270 (4.09)	238 (4.14)

## EXPERIMENTAL

M.ps are uncorrected and were obtained on an electrothermal capillary m.p. apparatus. Elemental analyses were supplied by the microanalysis laboratories at the University of Cairo, U.A.R. UV spectra were measured in 95% MeOH, using a Beckman DK spectrophotometer. The IR spectra were recorded on a Beckmann IR-4 (nujol mulls or KBr).

*Cyanoacetarylamides.* Cyanoacetanilide,<sup>13a</sup> cyanoacet-*p*-toluidide,<sup>13a</sup> cyanoacet-*m*-toluidide,<sup>13a</sup> cyanoacet-*p*-aniside,<sup>13b</sup> cyanoacet-*p*-chloroanilide,<sup>13c</sup> cyanoacet-*m*-chloroanilide,<sup>13c</sup> and cyanoacet-*N*-methyl-anilide<sup>13d</sup> were prepared by the literature methods. The following cyanoacetarylamides are new and were prepared by the general method.<sup>13a</sup> Cyanoacet-*m*-aniside was obtained in 60% yield, crystallized from EtOH, m.p. 158–159° (Calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 63.16; H, 5.26; N, 14.74. Found: C, 63.40; H, 5.36; N, 14.81%). Cyanoacet-*m*-nitroanilide (50%) was crystallized from EtOH, m.p. 171° (Calcd. for C<sub>9</sub>H<sub>7</sub>N<sub>3</sub>O<sub>3</sub>: C, 52.68; H, 3.42; N, 20.48. Found: C, 52.70; H, 3.39; N, 20.26%).

Cyanoacet-*p*-nitroanilide was better prepared by the following method. To a solution of cyanoacetic acid (13.0 g, 0.18 mole) in 125 ml. of dry ether, was added PCl<sub>5</sub> (35.5 g, 0.2 mole) in one portion. The mixture was stirred for 15 min at room temp., and the solvent together with POCl<sub>2</sub> formed removed under reduced pressure. The pale yellow oil left behind was diluted with 25 ml of dry C<sub>6</sub>H<sub>6</sub> and treated with *p*-nitroaniline (20 g, 0.15 mole). The mixture was refluxed for 12 hr. then cooled. The crude solid formed was collected, and recrystallized from MeOH to give 25 g. (82%) of pure cyanoacet-*p*-nitroacetanilide as pale yellow needles, m.p. 225° (lit.<sup>13e</sup> m.p. 225–227° for the compound prepared by condensing cyanoacetyl dimethyl pyrazolone with *p*-nitroaniline).

*Preparation of the Arylazo Cyanoacetarylamides*

A solution of 0.005 mole of the appropriate cyanoacetarylamide (I–II) in 100 ml of ethanol was stirred at room temperature for 10 minutes with 1.3 g of sodium acetate. The mixture was then chilled to 0–5°, vigorously stirred and treated dropwise with a cold (0–5°) solution of diazonium salt prepared by diazotizing 0.005 mole of the arylamine in 6 ml. of 6 M hydrochloric acid with 0.7 g (0.01 mole) of sodium nitrite in 10 ml of water. After the addition, the reaction mixture was left to stand overnight in the refrigerator. The resulting solid (usually colored) was filtered and washed thoroughly with water. The crude product was recrystallized from ethanol (or acetic acid). The compounds prepared are listed in Table 5.

*The coupling reactions of Arylazocyanoacetarylamides in NaOH.* A solution of 1.4 g (0.005 mole) of phenylazocyanoacetanilide (VIa) in 50 ml. of EtOH was mixed with 50 ml. NaOH aq. (0.4 g of NaOH). The solution was cooled to below 5°. A benzenediazonium chloride solution prepared from 0.46 g (0.005 mole) of aniline was added dropwise with stirring. After addition, the solution was stirred for 20 min and left to stand overnight in a refrigerator. The precipitate was filtered, washed with H<sub>2</sub>O, recrystallization from glacial AcOH to give 1.0 g (74% yield) of orange needles, m.p. 160°, 3-cyano-1,5-diphenylformazan (IXa). M.m.p. with an authentic sample, prepared from coupling cyanoacetic acid with two equivalents of benzenediazonium chloride as previously described,<sup>7a</sup> showed no depression. The IR and UV spectra of IXa were identical with those of the authentic sample.

When each of the phenylazo derivatives VIIb, VIIh or VIIn was coupled with benzenediazonium salt using the same procedure as for VIa, 3-cyano-1,5-diphenylformazan (IXa) was the only product obtained.



TABLE 5. ARYLACETANOCETARYLAMIDES  $N \equiv C - C(=N, NHC_6H_4R')CON(R)C_6H_4 - R''$

Compound No.	R	R'	R''	Yield %	M.p.	Formula	C. %		H. %		N. %		Hal. %	
							Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Via	H	H	H	78	199-200									
Vib	H	4-CH <sub>3</sub>	H	81	207-208	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O	69.05	69.21	5.07	4.91	20.13	20.31	—	—
Vic	H	3-CH <sub>3</sub>	H	63	205-206	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O	69.06	68.96	5.07	5.32	20.13	20.08	—	—
Vid	H	2-CH <sub>3</sub>	H	67	164	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O	69.05	68.87	5.07	5.10	20.13	20.31	—	—
Vle	H	4-CH <sub>3</sub> O	H	68	165	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>	65.29	65.61	4.79	4.70	19.04	18.92	—	—
Vlf	H	3-CH <sub>3</sub> O	H	83	180	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>	65.29	65.49	4.79	4.80	19.04	19.35	—	—
Vlg	H	2-CH <sub>3</sub> O	H	74	176	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>	65.29	64.94	4.79	4.82	19.04	19.06	—	—
Vih	H	4-Cl	H	60	212	C <sub>15</sub> H <sub>11</sub> ClN <sub>4</sub> O	60.30	59.96	3.71	3.73	18.76	18.73	11.87	11.82
Vii	H	3-Cl	H	43	230-231	C <sub>15</sub> H <sub>11</sub> ClN <sub>4</sub> O	60.30	60.21	3.71	4.01	18.76	18.62	11.87	11.68
Vlj	H	2-Cl	H	69	150-151	C <sub>15</sub> H <sub>11</sub> ClN <sub>4</sub> O	60.30	60.54	3.71	3.90	18.76	18.56	11.87	11.84
Vlk	H	4-Br	H	74	217	C <sub>15</sub> H <sub>11</sub> BrN <sub>4</sub> O	52.49	52.31	3.23	3.11	16.33	16.19	23.29	23.16
Vll	H	3-Br	H	71	277	C <sub>15</sub> H <sub>11</sub> BrN <sub>4</sub> O	52.49	52.36	3.23	3.13	16.33	16.51	23.29	23.43
Vlm	H	4-NO <sub>2</sub>	H	60	261-263	C <sub>15</sub> H <sub>11</sub> N <sub>5</sub> O <sub>3</sub>	58.25	58.63	3.59	3.67	22.65	22.28	—	—
Vln	H	3-NO <sub>2</sub>	H	53	205	C <sub>15</sub> H <sub>11</sub> N <sub>5</sub> O <sub>3</sub>	58.25	58.63	3.59	3.59	22.65	22.85	—	—
Vlo	H	2-OH	H	80	202	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub>	64.28	64.21	4.32	4.40	19.99	19.95	—	—
Vlp	H	2-CO <sub>2</sub> H	H	82	241	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub>	62.33	62.27	3.92	3.91	18.17	17.89	—	—
Vlq	H	4-(CH <sub>3</sub> ) <sub>2</sub> N	H	88	198	C <sub>17</sub> H <sub>17</sub> N <sub>5</sub> O	66.43	67.05	5.58	5.69	22.79	22.40	—	—
Vlrb	H	H	4-CH <sub>3</sub>	81	196	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O	69.05	69.18	5.07	5.37	20.13	20.21	—	—
Vlrc	H	H	3-CH <sub>3</sub>	79	162	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O	69.05	69.08	5.07	5.17	20.13	20.54	—	—
Vlrd	H	H	4-CH <sub>3</sub> O	70	201	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>	65.29	65.20	4.79	4.49	19.04	18.98	—	—
Vlre	H	H	3-CH <sub>3</sub> O	61	185	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>	65.29	65.34	4.79	4.92	19.04	19.20	—	—
Vlrf	H	H	4-Cl	69	225	C <sub>15</sub> H <sub>11</sub> ClN <sub>4</sub> O	60.30	60.21	3.71	3.77	18.78	18.98	11.87	11.87
Vlrg	H	H	3-Cl	70	208	C <sub>15</sub> H <sub>11</sub> ClN <sub>4</sub> O	60.30	59.98	3.71	4.00	18.78	18.97	11.87	11.57
Vlri	H	H	4-NO <sub>2</sub>	88	259	C <sub>15</sub> H <sub>11</sub> N <sub>5</sub> O <sub>3</sub>	58.25	58.24	3.59	3.89	22.65	22.52	—	—
Vlrii	H	H	3-NO <sub>2</sub>	80	217	C <sub>15</sub> H <sub>11</sub> N <sub>5</sub> O <sub>3</sub>	58.25	58.16	3.59	3.96	22.65	22.61	—	—
Vlriii	CH <sub>3</sub>	H	H	79	160	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O	69.05	68.89	5.07	5.16	20.13	20.22	—	—

TABLE 6. 3-CYANO-1,5-DIARYLFORMAZANS R C<sub>6</sub>H<sub>4</sub>NH.N=C(CN)N=N.C<sub>6</sub>H<sub>4</sub>R'

Compound No.	R'	R''	Yield %	M.p. (Lit. mp.)	Formula	C, %		H, %		N, %		Hal, %	
						Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
IXa	H	H	74	160 (158) <sup>7a</sup>									
IXb	4-Br	4-Br	70	260 (260) <sup>7b</sup>									
IXc	2-CO <sub>2</sub> H	2-CO <sub>2</sub> H	81	225 (225-227) <sup>7c</sup>									
IXd	4-NO <sub>2</sub>	4-NO <sub>2</sub>	53	247 (247-248) <sup>7d</sup>									
IXe	H	4-NO <sub>2</sub>	63	244	C <sub>14</sub> H <sub>10</sub> N <sub>6</sub> O <sub>2</sub>	57.14	56.98	3.40	4.02	28.57	28.49		
IXf	4-NO <sub>2</sub>	4-Br	71	248-250	C <sub>14</sub> H <sub>8</sub> BrB <sub>6</sub> O <sub>2</sub>	45.04	44.97	2.41	2.18	22.52	22.21	21.45	21.40
IXg	H	4-CH <sub>3</sub> O	64	184-186	C <sub>13</sub> H <sub>13</sub> N <sub>5</sub> O	64.52	64.61	4.66	4.60	25.09	24.98		
IXh	4-CH <sub>3</sub> O	4-CH <sub>3</sub> O	67	180	C <sub>16</sub> H <sub>15</sub> N <sub>5</sub> O <sub>2</sub>	62.14	62.11	4.85	4.37	22.69	22.57		
IXi	4-NO <sub>2</sub>	4-CH <sub>3</sub> O	69	220	C <sub>13</sub> H <sub>12</sub> N <sub>6</sub> O <sub>3</sub>	55.56	55.29	3.70	3.92	25.92	25.87		
IXj	4-Br	4-CH <sub>3</sub> O	81	238-239	C <sub>15</sub> H <sub>12</sub> BrN <sub>5</sub> O	50.28	50.07	3.35	3.17	19.56	19.49	22.35	22.13
IXk	H	4-Br	72	230	C <sub>14</sub> H <sub>10</sub> N <sub>5</sub> Br	51.22	51.19	3.03	2.98	21.34	21.08	24.41	24.52

TABLE 7. ARYLazo DERIVATIVES OF IMINOACYL AND ACYL-ACETAMIDES R...CY.C(=N NHCH<sub>6</sub>H<sub>4</sub>R or H)CO—NHC<sub>6</sub>H<sub>5</sub>

Compound No.	Y	R	R'	Yield %	M.p. (lit. mp.)	Formula	C, %		H, %		N, %	
							Calc.	Found	Calc.	Found	Calc.	Found
Xa	NH	C <sub>6</sub> H <sub>5</sub>	H	78	137	C <sub>21</sub> H <sub>18</sub> N <sub>4</sub> O	73.68	73.60	5.26	5.11	16.37	16.19
XIa	O	C <sub>6</sub> H <sub>5</sub>	H	70	160 (159-160) <sup>5</sup>							
Xb	NH	C <sub>6</sub> H <sub>5</sub>	4-CH <sub>3</sub>	80	172	C <sub>22</sub> H <sub>20</sub> N <sub>4</sub> O	73.95	73.69	5.60	5.32	15.68	15.59
XIb	O	C <sub>6</sub> H <sub>5</sub>	4-CH <sub>3</sub>	72	179 (179) <sup>15</sup>							
Xc	NH	CH <sub>3</sub>	H	80	170	C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O	68.57	68.29	5.71	5.63	20.00	19.92
XIc	O	CH <sub>3</sub>	H	60	107 (106-107) <sup>16</sup>							
Xd	NH	C <sub>2</sub> H <sub>5</sub>	H	85	159	C <sub>17</sub> H <sub>18</sub> N <sub>4</sub> O	69.39	69.01	6.12	6.24	19.04	19.13
XId	O	C <sub>2</sub> H <sub>5</sub>	H	75	103-104	C <sub>17</sub> H <sub>17</sub> N <sub>4</sub> O <sub>2</sub>	69.15	69.01	5.76	5.81	14.23	14.12

Following the above general procedure the other arylazocycanoacetarylamides (VIc, VIk and VI m) were coupled with various diazonium salts (Table 6).

In NaOAc buffer. Using the procedure for NaOH solution the coupling reaction of benzenediazonium salt to the arylazocycanoacetarylamides (VIa, VIb and VIk) did not occur. Unreacted arylazocycanoacetarylamides were recovered.

*Reactions of arylazocycanoacetarylamides with Grignard reagents.* To a cold Grignard reagent (prepared from 1.0 g Mg and the proper quantity of the alkyl or aryl halide in 50 ml of ether), was added a solution of each of arylazocycanoacetarylamides (VIa, VIIb) 0.005 mole in 50 ml ether. The mixture was refluxed for two hr, then left overnight at room temp. The mixture was decomposed by aqueous saturated  $\text{NH}_4\text{Cl}$ , and the ether layer separated. The aqueous layer was extracted three times with 10 ml portions of ether, the extracts combined, dried ( $\text{Na}_2\text{SO}_4$ ) and filtered. The residue, left after evaporating the solvent, was triturated with petroleum ether (40/60°). The resulting solid was recrystallized from EtOH. The arylazo derivatives of iminoacylacetanilides (Xa-d) prepared are pale yellow, insoluble in NaOH, and give no color with alcoholic  $\text{FeCl}_3$ . Table 7, summarizes the physical constants.

*Acid hydrolysis of  $\alpha$ -arylazoiminoacylacetanilides.* Phenylazo iminobenzoyl acetanilide (Xa) (0.005 mole) was suspended in 20 ml of HCl (10 M). The suspension was refluxed for 30 min. and cooled. The product was filtered and washed with  $\text{H}_2\text{O}$ . Recrystallization from EtOH gave 0.8 g. (70%) of phenylazobenzoylacetanilide (XIa) m.p. 160°. M.m.p. with an authentic sample (prepared from coupling of benzenediazonium chloride with benzoylacetanilide)<sup>5</sup> showed no depression (lit.<sup>5</sup> m.p. 159–160°).

The other arylazoiminoacylacetanilides (Xb-d) were similarly hydrolyzed and the following arylazoacylacetanilides (XIb-d)  $\text{R-COC} (=N\cdot\text{NHCONH Ar})\text{CONHC}_6\text{H}_5$  were obtained: XIb, R =  $\text{C}_6\text{H}_5$ , Ar = 4- $\text{CH}_3\text{C}_6\text{H}_4$ , m.p. 179° (72%) m.m.p. 178–179° (lit.<sup>5</sup> 179°); XIc, R =  $\text{CH}_3$ , Ar =  $\text{C}_6\text{H}_5$ , m.p. 107° (60%), m.m.p. 106° (lit.<sup>15</sup> 106–107°); XI d, m.p. 103–104° (75%). (Calcd. for  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2$ : C, 69.15; H, 4.30; N, 10.67. Found: C, 69.01; H, 4.21; N, 10.55%.)

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