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Reactions of 3-nitro-1,5-diarylformazans **1a-c** with carbanions of acetylacetone, dibenzoylmethane, acetoacetanilide, benzoylacetonitrile, ω -benzenesulfonylacetoephone and malononitrile yielded the corresponding 3-arylazopyrazole derivatives **4-9** respectively. Reactions of **1** with nucleophiles result in displacement of the nitro group and the formation of the corresponding 3-substituted formazans **10-13**. Treatment of **1** with potassium thiocyanate gave, however, 5-imino-2-arylazo-1,3,4- Δ^2 -thiadiazolines **14**. Structural assignments have been made on the basis of spectral and elemental analyses, chemical behaviour and alternate synthesis wherever possible.

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Introduction.

Our interest in the synthesis of 3-arylazopyrazoles and 2-arylazo-1,3,4-thiadiazolines has prompted us to examine the reactivity of 3-nitro-1,5-diarylformazans **1** with carbanions and thiocyanate anion. Compounds of type **1** are, formally, related to α -nitrohydrazones **2**, which have recently proved to be useful in the synthesis of heterocycles [2-6]. In spite of the very large amount of literature [7,8] on formazans, very little attention, if there is any, has been given to the use of **1** in heterocyclic synthesis until recently.

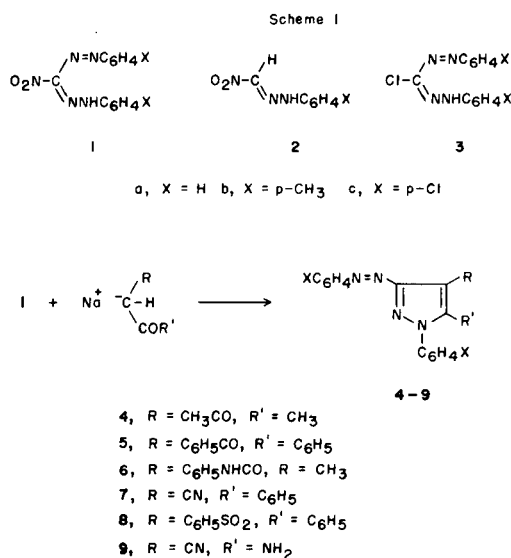
Furthermore, in contrast to 5-arylazopyrazoles [9] and 4-arylazopyrazoles [10] no convenient route has yet been reported for synthesis of 3-arylazopyrazoles [11]. In addition 2-arylazo-1,3,4-thiadiazolines have not yet been reported. Here we wish to report a convenient synthetic procedure using **1** as precursors of these systems.

Results and Discussion.

Addition of 3-nitroformazan (**1a**) to a solution of the sodium salt of acetylacetone in ethanol at room temperature gave readily one separable product **4a** which analyzed for $C_{18}H_{16}N_4O$. The ir spectrum of **4a** exhibits an absorption band at 1660 cm^{-1} characteristic of conjugated acetyl carbonyl [12] and another absorption at 1590 cm^{-1} corresponding to a C=N linkage of a pyrazole ring [12]. The pmr spectrum of **4a** in deuterated chloroform reveals two singlets at δ 2.5 (3H), and 2.7 (3H) ppm assignable to the CH_3CO and vinyl methyl groups, respectively. Also, it shows a multiplet at δ 7.2-8.0 (10H) ppm corresponding to the aromatic protons. From these results, compound **4a** can be assigned the structure of 1-phenyl-3-phenylazo-4-acetyl-5-methylpyrazole. Compound **1b** reacted similarly with acetylacetone in the presence of sodium ethoxide and gives the corresponding pyrazole derivative **4b**.

Similar treatment of **1** with equivalent amounts of the sodium salts of dibenzoylmethane, benzoylacetonitrile, acetoacetanilide, ω -benzenesulfonylacetoephone and mal-

ononitrile gave **5-9** in 70-75% yield, respectively (Scheme 1). The spectral properties (Table 1) and the elemental



analysis data (Table 3) of these new pyrazole derivatives were in agreement with their assigned structures. Alternatively, the products **4-9** were conveniently prepared by reaction of 3-chloro-1,5-diarylformazans with the appropriate active methylene compounds (see Experimental).

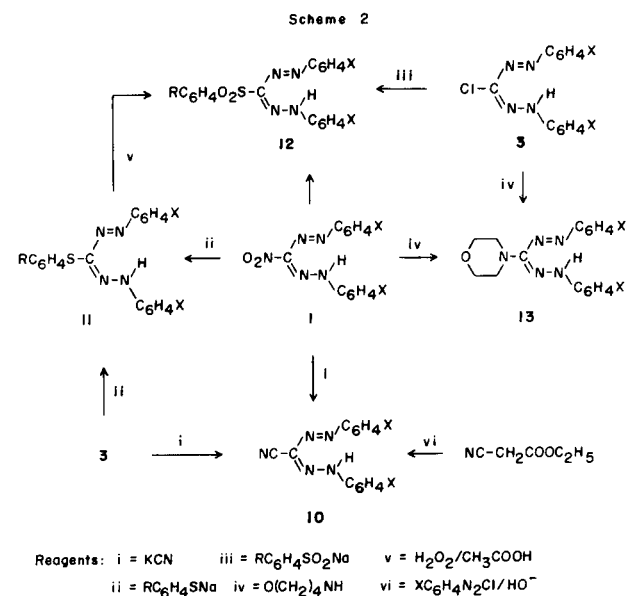
It has been reported [8] that the nitro group in **1** can be replaced by NH_2 , SH and OH groups. In this work, it was found that treatment of **1** with other nucleophiles such as potassium cyanide, sodium thiophenolate, sodium benzenesulfinate, and morpholine in ethanol readily gave the substitution products **10-13**, respectively (Scheme 2). The identity of the product in each case was established on the basis of elemental analysis, spectral data (Tables 2, 4) and by alternate synthesis from 3-chloro-1,5-diarylformazans [13] (see Experimental). Also, the product **10** obtained from **1a** with potassium cyanide was identical in all re-

Table 1
The Spectral Characteristics of the Products 4-9

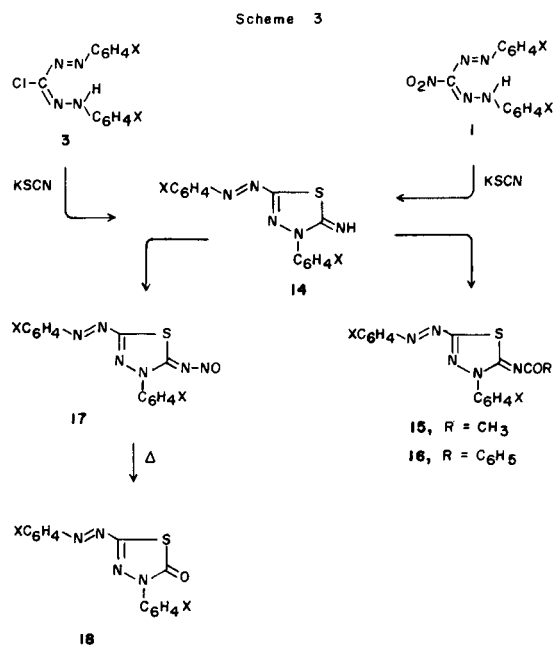
Compound No.	ν (assignment) cm^{-1} .	δ (assignment) ppm
4a	1660 (CO)	2.7 (3H, s, CH_3), 2.5 (3H, s, COCH_3), 7.2-8.0 (10H, m, ArH)
4b	1655 (CO)	2.4 (6H, s, 2CH_3), 2.6 (3H, s, CH_3), 2.5 (3H, s, COCH_3), 7.1-8.0 (8H, m, ArH)
5a	1670 (CO)	7.2-8 (20H, m, ArH)
5b	1660 (CO)	2.3 (6H, s, 2CH_3), 7.0-7.9 (18H, m, ArH)
6a	1660 (amide CO), 3310 (amide NH)	2.7 (3H, s, CH_3), 7.0-8.1 (16H, m, ArH and NH)
6b	1650 (amide CO), 3320 (amide NH), 2220 (C=N)	2.4 (6H, s, 2CH_3), 2.73 (3H, s, CH_3), 7.0-8.0 (14H, m, ArH and NH)
7a	2220 (C=N)	7.2-8.2 (15H, m, ArH)
8a	1155, 1310 (SO_2)	7.2-8.1 (20H, m, ArH)
9b	2220 (C=N), 3225, 3320, 3360 (NH_2)	2.4 (6H, s, 2CH_3), 4.72 (2H, s, NH_2), 7.1-8.0 (8H, m, ArH)

Table 2
The Spectral Characteristics of the Products 10-18

Compound No.	ν (assignment) cm^{-1}	δ (assignment) ppm
10b	2230 (C=N), 3230 (NH)	2.4 (6H, s, 2CH_3), 7.1-7.8 (8H, m, ArH), 13.0 (1H, s, NH)
11a	3250 (NH)	2.3 (6H, s, 2CH_3), 7.0-7.8 (13H, m, ArH), 9.3 (1H, s, NH)
12a	1145, 1320 (SO_2), 3020 (NH)	2.4 (6H, s, 2CH_3), 7.1-7.8 (13H, m, ArH), 12.85 (1H, s, NH)
12b	1150, 1320 (SO_2), 3030 (NH)	2.4 (6H, s, 2CH_3), 2.5 (3H, s, CH_3), 7.1-7.8 (12H, m, ArH), 12.8 (1H, s, NH)
14b	3320 (NH), 1620 (C=N)	2.43 (6H, s, 2CH_3), 7.2-8.0 (9H, m, ArH, NH)
15b	1635 (CO)	2.34 (3H, s, COCH_3), 2.41 (6H, s, 2CH_3), 7.0-8.5 (8H, m, ArH)
16b	1625 (CO)	2.41 (6H, s, 2CH_3), 7.1-8.2 (13H, m, ArH)
18b	1690 (CO)	2.4 (6H, s, 2CH_3), 7.2-8.0 (8H, m, ArH)



were consistent with their assigned structures (Tables 2,5). These structures were also confirmed by their reactions which are summarized in Scheme 3. Thus, **14** with acetic



spects with an authentic sample prepared from coupling of ethyl cyanoacetate with two equivalents of benzenediazonium chloride [14]. However reaction of **1** with two equivalents of potassium thiocyanate in ethanol gave products identified as 2-arylozo-5-iminothiadiazolines **14**. The latter were also obtained by the reaction of 3-chloroformazan **3** (Scheme 3). Both elemental and spectral data of **14**

Table 3
3-Arylazopyrazole Derivatives 4-9

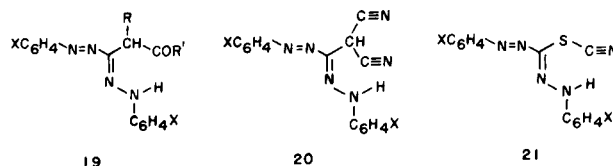
Compound No.	Mp, °C	Molecular Formula	Analysis		
			Calcd. C, %	(Found) H, %	(Found) N, %
4a	179 [a]	C ₁₈ H ₁₆ N ₄ O	71.05 (71.20)	5.30 (5.30)	18.42 (18.52)
4b	210	C ₂₀ H ₂₀ N ₄ O	72.26 (71.98)	6.06 (5.81)	16.86 (16.68)
5a	179	C ₂₆ H ₂₀ N ₄ O	78.49 (78.40)	4.70 (4.90)	13.08 (13.10)
5b	194	C ₃₀ H ₂₄ N ₄ O	78.92 (79.11)	5.30 (5.30)	12.27 (12.15)
6a	198	C ₂₃ H ₁₉ N ₅ O	72.42 (72.24)	5.02 (4.98)	18.36 (18.40)
6b	240	C ₂₅ H ₂₃ N ₅ O	73.33 (73.10)	5.66 (5.70)	17.10 (16.90)
7a	205 [b]	C ₂₂ H ₁₅ N ₅	75.63 (75.70)	4.33 (4.34)	20.04 (19.86)
8a	225	C ₂₇ H ₂₀ N ₄ SO ₂	69.81 (70.00)	4.34 (4.50)	12.06 (12.05)
9b	220	C ₁₈ H ₁₆ N ₆	68.34 (68.20)	5.10 (5.20)	26.56 (26.70)

[a] Lit mp 179° [23]. [b] Lit mp 204-205° [23].

anhydride in acetic acid and benzoyl chloride in pyridine gave the *N*-acetyl and *N*-benzoyl derivatives **15** and **16** respectively. Nitrosation of **14** yielded the *N*-nitroso derivatives **17** which decompose upon heating in xylene to give 2-arylazo-5-thiadiazolinones **18**.

In the light of the ease with which the nitro group in **1** is substituted by various nucleophiles, it is not unreasonable to propose that the formation of the products **4-8** proceeds

through acyclic intermediates of type **19**. The latter seem to undergo cyclization as soon as they are formed by the loss of the elements of water to give **4-8** [12]. Similarly, the formation of the pyrazole derivatives **9** and the thiadiazolines **14** seem to result from an intramolecular addition of the hydrazone NH to the nitrile group in the acyclic substitution intermediates **20** and **21** respectively [15,16].



EXPERIMENTAL

All melting points are uncorrected. The infrared spectra (potassium bromide disc) were recorded on a ZEISS spectrophotometer. The ¹H pmr spectra in deuterated chloroform were recorded on a Varian EM 390, 90 MHz spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed by the Microanalytical Laboratory, Cairo University, Giza, Egypt. 1,5-Diaryl-3-nitroformazans **1** [17-20] and 1,5-diaryl-3-chloroformazans **3** [21,22] were prepared as previously described.

Reaction of **1** with Active Methylene Compounds. General Procedure.

The appropriate active methylene compound (0.01 mole) was added to an ethanolic sodium ethoxide solution (prepared from sodium metal (0.23 g, 0.01 g-atom) and 50 ml of absolute ethanol). After stirring for 10 minutes, compound **1** (0.01 mole) was added and stirring was continued for further 30 minutes. The reaction mixture was then left overnight at room temperature. The precipitated product was collected by filtration. In some cases addition of water to the reaction mixture was necessary to effect precipitation. The crude pyrazole derivative was washed with water, dried and crystallized from methanol. The compounds **4-9** ob-

Table 4
3-Substituted-1,5-diarylformazans



Compound No.	Mp, °C	3-Y	X	S [a]	Molecular Formula	Analysis		
						Calcd. C, %	(Found) H, %	(Found) N, %
10a	230 [b]	CN	<i>p</i> -CH ₃	E	C ₁₆ H ₁₅ N ₅	69.29 (69.35)	5.45 (5.31)	25.25 (25.41)
10b	236 [c]	CN	<i>p</i> -Cl	A	C ₁₄ H ₉ Cl ₂ N ₅	52.85 (52.94)	2.85 (2.80)	22.01 (21.99)
11a	169	C ₆ H ₅ S	<i>p</i> -CH ₃	M	C ₂₁ H ₂₀ N ₄ S	69.97 (69.79)	5.59 (5.80)	15.54 (15.40)
11b	150	<i>p</i> -CH ₃ C ₆ H ₄ S	<i>p</i> -CH ₃	E	C ₂₂ H ₂₂ N ₄ S	70.56 (70.60)	5.92 (5.90)	14.96 (15.20)
12a	219 [d]	C ₆ H ₅ SO ₂	<i>p</i> -CH ₃	A	C ₂₁ H ₂₀ N ₄ O ₂ S	64.27 (64.20)	5.14 (5.20)	14.28 (14.11)
12b	215	<i>p</i> -CH ₃ C ₆ H ₄ SO ₂	<i>p</i> -CH ₃	A	C ₂₂ H ₂₂ N ₄ O ₂ S	65.00 (65.20)	5.46 (5.60)	13.78 (13.87)
13a	120 [a]	O(CH ₂) ₄ N	H	E	C ₁₇ H ₁₉ N ₅ O	66.00 (65.98)	6.19 (6.10)	22.63 (22.59)

[a] S = solvent of crystallization: A = acetic acid, E = ethanol, M = methanol. [b] Lit mp 216-217° [14]. [c] Lit mp 240-242° [14]. [d] Lit mp 210° [24]. [e] Lit mp 120-121.5° [13].

tained and their physical properties are listed in Tables 1 and 3. Repetition of the above procedure using the appropriate 3-chloro-1,5-diarylformazans **3** in place of 3-nitroformazans **1** gave products identical in all respects (spectra, mp, mixed mp) with **4-9**.

Table 5

2-Arylazo-1,3,4- Δ^2 -thiadiazoline Derivatives

Compound No.	Mp, °C	S [a]	Molecular Formula	Analysis		
				Calcd. (Found)		
				C, %	H, %	N, %
14b	205	E	C ₁₆ H ₁₅ N ₅ S	62.11 (62.10)	4.89 (4.90)	22.64 (22.57)
14c	228	X	C ₁₄ H ₉ Cl ₂ N ₅ S	48.01 (48.10)	2.59 (2.49)	20.00 (19.99)
15b	195	E	C ₁₈ H ₁₇ N ₅ OS	61.52 (61.49)	4.88 (4.80)	19.93 (19.85)
15c	205	E	C ₁₆ H ₁₁ Cl ₂ N ₅ OS	48.99 (49.05)	2.83 (2.77)	17.89 (17.62)
16b	220	A	C ₂₃ H ₁₉ N ₅ OS	66.81 (66.77)	4.63 (4.55)	16.94 (16.82)
16c	298	A	C ₂₁ H ₁₄ Cl ₂ N ₅ OS	55.39 (55.50)	3.10 (2.99)	15.38 (15.21)
17b	170	B	C ₁₆ H ₁₄ N ₆ OS	56.79 (56.77)	4.17 (4.08)	24.84 (24.78)
17c	208	E	C ₁₄ H ₉ Cl ₂ N ₆ OS	44.22 (44.30)	2.39 (2.34)	22.10 (22.09)
18b	185	E	C ₁₆ H ₁₄ N ₄ OS	61.91 (61.89)	4.55 (4.50)	18.05 (17.98)
18c	208	X	C ₁₄ H ₉ Cl ₂ N ₄ OS	47.87 (47.98)	2.30 (2.25)	15.95 (16.00)

[a] S = solvent of crystallization: A = acetic, B = benzene, E = ethanol, X = xylene.

Reactions of **1** or **3** with Nucleophiles.

Equimolecular quantities of **1** (or **3**) and the appropriate nucleophile (NaSAr, NaO₂SAr, NaCN, morpholine, or KSCN) (0.01 mole each) in ethanol (20 ml) were stirred for 0.5-2 hours and left overnight at room temperature. The product was collected, washed with water and crystallized from ethanol or acetic acid. In the case of the reaction with morpholine, the reaction mixture was refluxed for 3 hours. The compounds prepared **10-13** are listed in Tables 2,4.

Oxidation of **11**.

To a solution of **11** (7 mmoles) in acetic acid was added hydrogen peroxide solution (2 ml, 33%), and the mixture was left for two days at room temperature, then poured on water. The crude product was collected and crystallized from acetic acid to give the corresponding **12** in 73-78% yield. The melting point of a mixture of this product with that obtained from reaction of **1** and the appropriate sodium arenedisulfinate showed no depression.

Reaction of **1** with Potassium Thiocyanate.

To a suspension of **1** (0.005 mole) in ethanol (25 ml) was added potassium thiocyanate (0.97 g, 0.01 mole) stirring. The reaction mixture was refluxed for 6 hours and cooled. The precipitated solid was collected, washed with water, dried and finally crystallized from ethanol or xylene. The products **14** were obtained in 70-80% yield and their physical constants are given in Tables 2,5. Repetition of the above procedure using **3** in place of **1** yielded **14** (75% yield) identical in all respects with those obtained from **1** and potassium thiocyanate.

Acylation of **14**.

Compound **14** (1 g) was refluxed in acetic anhydride (20 ml) for 15 min-

utes, cooled and poured on crushed ice. The crude solid which precipitated was collected and crystallized from ethanol to give the corresponding *N*-acetyl derivative **15**. Benzoylation of **14** was effected by refluxing equivalent amount of **14** and benzoyl chloride (0.001 mole) in pyridine (15 ml) for 20 minutes, cooled and poured on ice cold dilute hydrochloric acid. Crystallization from acetic acid gave **18** in 65-78% yield (Tables 2,5).

Nitrosation of **14**.

A solution of **14** (1 g) in acetic acid (30 ml) was treated with a saturated aqueous solution of sodium nitrite while stirring 1 hour. The product was collected and crystallized from ethanol. Compound **17** was obtained in almost quantitative yield. The compounds prepared are listed in Table 5.

Thermolysis of **17**.

Compound **17** (1.0 g) was refluxed in xylene (40 ml) for 2 hours and left overnight at room temperature. The solvent was removed under reduced pressure, and ethanol was added to the residue. The solid formed was collected and crystallized from ethanol to give **18** in 65% yield (Table 5).

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