Synthesis of 1-Aryl-5-arylazo-3-phenylsulfonyl-pyrazol-4-ols from 1-Bromo-3-phenylsulfonyl-2-propanone

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Received February 9, 1988

Treatment of 1-bromo-3-phenylsulfonyl-2-propanone (**1**) with arenediazonium chloride gave 1-aryl-5-arylazo-3-phenylsulfonylpyrazol-4-ols **5a-h** in 13-48% yields.

J. Heterocyclic Chem., **25**, 1219 (1988).

During the course of our investigation on the synthesis of heterocycles using sulfone derivatives, we have already reported the preparation of 5-sulfonylpyrimidines [1], 4-sulfonylpyrazoles, and 4-sulfonylisoxazoles [2] starting from β-keto-β-sulfonylenamines. Now we have become interested in the possibility that 1-halogeno-3-phenylsulfonyl-2-propanones **1** could serve as useful precursors for the synthesis of heterocycles. In spite of their polyfunctionality, little work has appeared dealing with reactivities of **1**. Attempted nucleophilic substitution of chlorine of **1b** by sodium methoxide resulted only in the formation of methyl phenyl sulfone [3-4]. Recently synthesis of enantiomerically pure 2,5-disubstituted tetrahydrofurans [5] and (4*S*)-2-alken-4-olides [6] have been accomplished by use of **1b**. We have examined the reactivities of **1a** [7] and found a route to 1-aryl-5-arylazo-3-phenylsulfonylpyrazol-4-ols **5**, a new class of pyrazole derivatives [8-9].

Reaction of **1a** with arenediazonium chloride in a usual manner followed by separation on column chromatography afforded pyrazoles **5a-h** in 13-48% yields (Scheme 1). The structures of **5** were established on the basis of the spectral data as shown in Table 1 and 2, and of preparation of some derivatives. Although the analytical and mass spectral data confirmed the molecular formulas corresponding to **5**, three tautomeric structures **5**, **6**, and **7** are possible in this pyrazole series (Scheme 2). 4-Arylazo-5-pyrazolones and 4-arylazo-3-pyrazolones are reported to exist in the hydrazone form **9** and hydroxy form **10**, respectively, forming intramolecular hydrogen bond [10]. The carbonyl absorptions and the methine proton resonances originated from the methylenes in **1a** were not observed in the ir and nmr spectra of the products, respectively. Thus, the presence of the tautomers **6** and **7** was excluded for the products. This conclusion is consistent with the reports that 5-arylazo-4-pyrazolones are present in the hydroxy form **8** [11-12]. Formation of pyrazolones **5** could be explained as follows: the initially formed hydrazones **2** cyclized on elimination of hydrogen bromide to 4-pyrazolones **3** or tautomeric pyrazol-4-ols **4**, which were further attacked by diazonium salt to yield **5**.

Since the hydroxyl absorptions did not appear appreciably in the ir spectra of **5**, further structural confirmation was undertaken (Scheme 3). Treatment of **5a** in acetic anhydride at 100° gave acetate **11** in 79% yield. The azo group of **5a** could be reduced on treatment with tin in hydrochloric acid at room temperature to yield 5-amino-pyrazol-4-ol (**12**) in 73% yield. The existence of an amino group in **12** was proved by ready formation of benzilidene derivative **13** in 94% yield on addition of benzaldehyde to an ethanolic solution of **12**. In contrast to **5a**, a distinct ab-

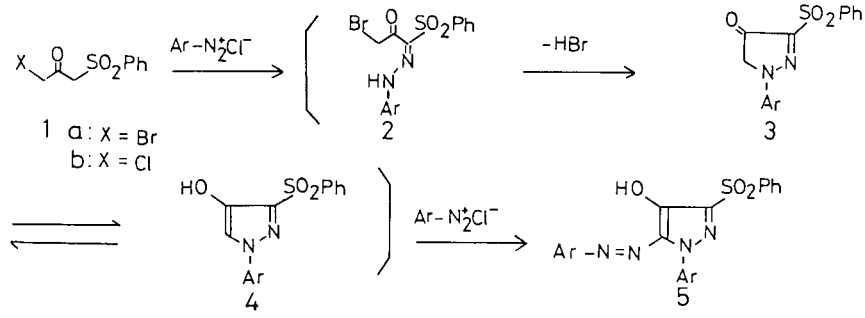
Table 1

Physical Properties of Compounds **5**, **11**, **12**, and **13**

	Yields (%)	Mp (°C) (Solvent)	Molecular Formula (Molecular Weight)	Elemental Analysis Calcd (%) C	Calcd (%) H	Found (%) C	Found (%) H
5a	30	181-183 (1-propanol)	$C_{21}H_{16}O_3N_4S$ (404.4)	62.37	3.99	62.46	4.00
5b	14	200-202 (1-propanol)	$C_{23}H_{20}O_3N_4S$ (432.5)	63.87	4.66	64.11	4.72
5c	23	200-202 (methanol)	$C_{21}H_{14}F_2O_3N_4S$ (440.4)	57.27	3.20	57.40	3.34
5d	36	224-227 (chloroform)	$C_{21}H_{14}Cl_2O_3N_4S$ (473.3)	53.29	2.98	53.09	3.10
5e	30	186-189 (methanol)	$C_{21}H_{14}Cl_2O_3N_4S$ (473.3)	53.29	2.98	53.53	3.13
5f	48	213-215 (chloroform)	$C_{21}H_{12}Cl_4O_3N_4S$ (542.2)	46.52	2.23	46.73	2.40
5g	34	224-227 (benzene)	$C_{21}H_{14}Br_2O_3N_4S$ (562.2)	44.86	2.51	44.73	2.56
5h	13	260-262 (chloroform)	$C_{21}H_{12}Br_4O_3N_4S$ (720.0)	35.03	1.68	35.01	1.76
11	79	151-153 (methanol)	$C_{23}H_{16}O_4N_4S$ (446.4)	61.88	4.06	62.15	4.06
12	73	171-173 (1-propanol)	$C_{15}H_{13}O_3N_3S$ (315.3)	57.14	4.16	57.60	4.27
13	94	196-198 (ethanol)	$C_{22}H_{17}O_3N_3S$ (403.5)	65.49	4.25	65.78	4.27

Compounds **5a-h** were red needles, **11** was orange needles, and **12-13** were white needles.

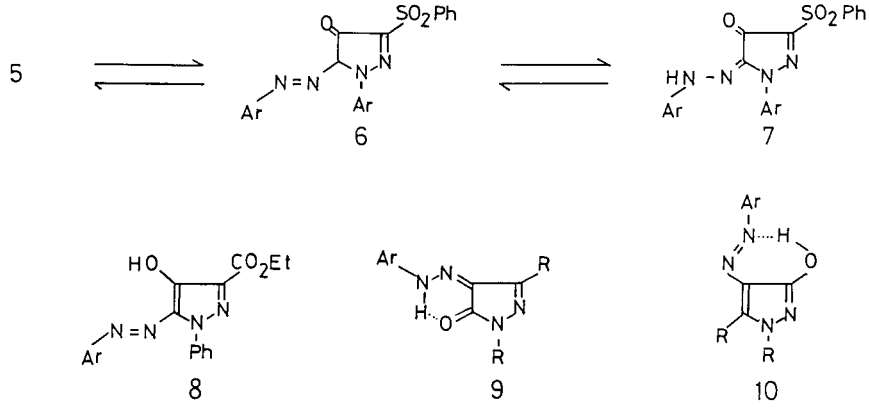
Scheme 1



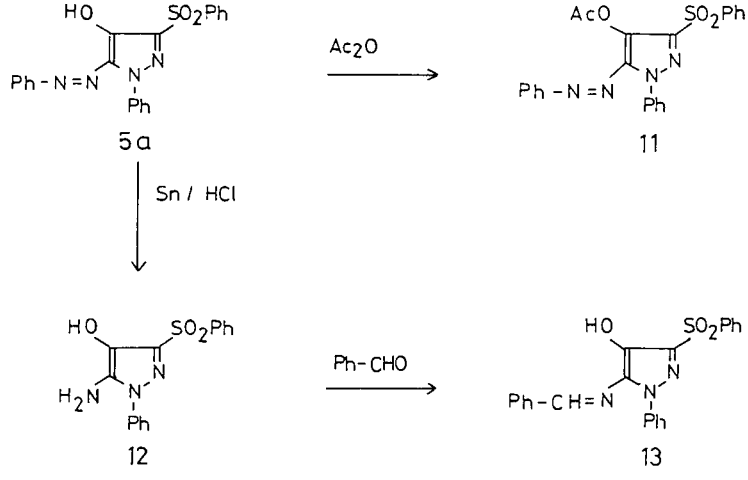
2-5	Ar
a	C_6H_5
b	4-Me C_6H_4
c	4-F C_6H_4
d	4-Cl C_6H_4

2-5	Ar
e	3-Cl C_6H_4
f	3,4-$Cl_2C_6H_3$
g	4-Br C_6H_4
h	2,4-$Br_2C_6H_3$

Scheme 2



Scheme 3



sorption of the hydroxyl group was observed in the ir spectrum of **13**. Satisfactory analytical and spectral data were obtained for these derivatives and are shown in Table 1 and 2.

Table 2

Spectral Data of Compounds **5**, **11**, **12**, and **13**

	Ms m/z (M^+)	IR [1] cm^{-1}			^{1}H-NMR δ, ppm
5a	404	1580	1540	1490	7.44-8.31 (m, ArH) [2]
5b	432	1590	1535	1500	2.41 (s, 6H, $-CH_3$), 7.20-8.27 (m, 13H, ArH) [2]
5c	440	1580	1545	1505	
5d	472	1565	1540	1480	
5e	472	1630	1585	1540	
5f	540	1630	1540	1470	
5g	560	1560	1540	1480	
5h	716	1540	1470	1440	
11	446	1775	1750	1580	2.32 (s, 3H, $-CH_3$), 7.33-8.14 (m, 15H, ArH) [2]
		1485	1460	1440	
12	315	3450	3350	3050	7.24-8.09 (m, ArH) [3]
		1620	1590	1485	
13	403	3400	1590	1560	7.37-8.19 (m, 15H, ArH), 9.18 (s, 1H, N=CH-) [2]
		1475	1440	1400	

[1] Potassium bromide. [2] In chloroform-d. [3] In acetone-d_6.

EXPERIMENTAL

Melting points were determined on a Yanagimoto micromelting apparatus. The ^{1}H-nmr, ir, and mass spectra were measured with a JEOL JNM-PMX 60, a JASCO A-102, and a JEOL JMS DX-300 spectrometer respectively. Microanalysis was performed with a Shimadzu UM-3B microanalyzer. The starting material **1a** was prepared according to the literature [7].

1-Phenyl-5-phenylazo-3-phenylsulfonylpyrazol-4-ol (**5a**).

A solution of sodium acetate (200 mg) in aqueous 1*N* sodium hydroxide (20 ml) was added to a solution of **1a** (277 mg, 1.0 mmole) in methanol (20 ml) and the mixture was stirred vigorously at 0-5°. To this mixture a solution of diazonium chloride prepared in a usual manner from aniline (2.5 mmoles), 1*N* hydrochloric acid (20 ml), and sodium nitrite (2.5 mmoles) was added dropwise during about 20 minutes. After additional stirring for 3 hours, the precipitate was collected by filtration and subjected to column chromatography on silica gel with chloroform as eluent. The red coloured fraction was collected to afford **5a** (121 mg, 30% yield). Compounds **5b-h** were prepared in a similar manner.

4-Acetoxy-1-phenyl-5-phenylazo-3-phenylsulfonylpyrazole (**11**).

A mixture of **5a** (101 mg, 0.25 mmole) in acetic anhydride (5 ml) was stirred at 100° for 3 hours. After cooling, the mixture was poured into water (50 ml). The resulting precipitate was collected by filtration and recrystallized from methanol to give **11** (88 mg, 79% yield).

5-Amino-1-phenyl-3-phenylsulfonylpyrazol-4-ol (**12**).

To a stirred mixture of **5a** (101 mg, 0.25 mmole) and powdered tin (163 mg, 1.4 mmoles) in methanol (10 ml), diluted hydrochloric acid (prepared from 0.21 ml of concentrated hydrochloric acid and 5 ml of water) was added at room temperature. After additional stirring for 30 to 45 minutes, the reaction mixture turned colourless. The solvent was removed, and the residue was extracted with water and chloroform. The residue obtained from the chloroform layer was recrystallized from 1-propanol to give **12** (57 mg, 73% yield).

5-(*N*-Benzylideneamino)-1-phenyl-3-phenylsulfonylpyrazol-4-ol (**13**).

To a stirred mixture of **12** (78 mg, 0.25 mmole) in ethanol (15 ml), benzaldehyde (0.025 ml, 0.26 mmole) was added at room temperature. The precipitate which formed after several minutes was collected by filtration to yield **13** (95 mg, 94% yield).

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