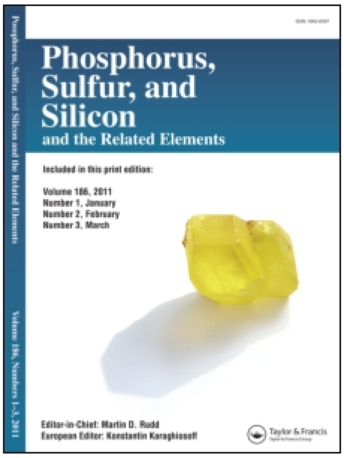

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REACTION OF HYDRAZONOYL HALIDES WITH 2,4-DIOXOTETRAHYDROTHIAZOLE-5-THIOCARBOXANILIDES

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Reaction of 3-phenyl-2,4-dioxotetrahydrothiazole-5-thiocarboxanilides 3 with hydrazonoyl halides 4 in N,N-dimethylformamide in the presence of potassium hydroxide yielded the thiadiazoline derivatives 7 and **13**. The mechanism of formation of the latter products is discussed.

Key words: Heterocycles, thiocarboxanilides, hydrazonoyl halides, NMR spectra.

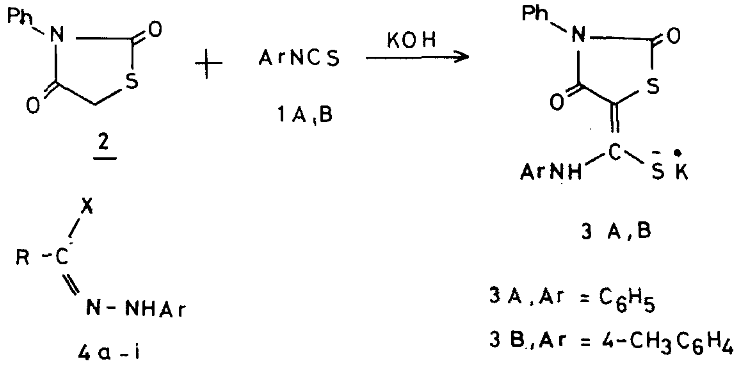
INTRODUCTION

In continuation of our work on hydrazonoyl halides,[1–3] we wish to report the results of our study of the reactions of 3-phenyl-2,4-dioxotetrahydrothiazole-5-thiocarboxanilides 3A,B with the hydrazonoyl halides **4**. Such reactions have not yet been studied although there are numerous reports on reactions of hydrazonoyl halides with various heterocyclic ring systems.[4]

RESULTS AND DISCUSSION

The intermediates 3A and 3B were prepared by reacting 2,4-dioxothiazolidine **2** with aryl isothiocyanates **1A,B** in N,N-dimethylformamide in the presence of potassium hydroxide (Scheme 1).

Treatment of **3A** with the hydrazonoyl halides **4a–c** in N,N-dimethylformamide afforded, in each case, one isolable product as evidenced by tlc analysis. Both mass spectral and elemental analyses data of the products isolated are compatible with the two possible structures **7** and **10** (Scheme 2). However, the latter structure **10** was discarded for the reaction products on basis of chemical evidence. Thus, the reaction products were recovered unchanged after treatment with mercuric oxide in boiling acetic acid. Such treatment is expected to convert **10**, if present, into **11**. Furthermore, reactions of acyclic ketothioanilides **12** with **4** have been reported to give 2-arylidene 1,3,4-thiadiazoline derivatives.[5] On the basis of these findings the products isolated from the studied reactions were assigned the structure **7**. This



	R / Ar / X
4a	C_6H_5 / C_6H_5 / Cl
4b	$C_6H_5CH=CH$ / C_6H_5 / Cl
4c	2-thienyl / $4\text{-}NO_2C_6H_4$ / Cl
4d	CH_3CO / C_6H_5 / Cl
4e	C_2H_5OCO / C_6H_5 / Cl
4f	C_6H_5CO / C_6H_5 / Br
4g	C_6H_5 CONH / C_6H_5 / Cl
4h	2-thienoyl / C_6H_5 / Br
4i	2-naphthoyl / C_6H_5 / Br

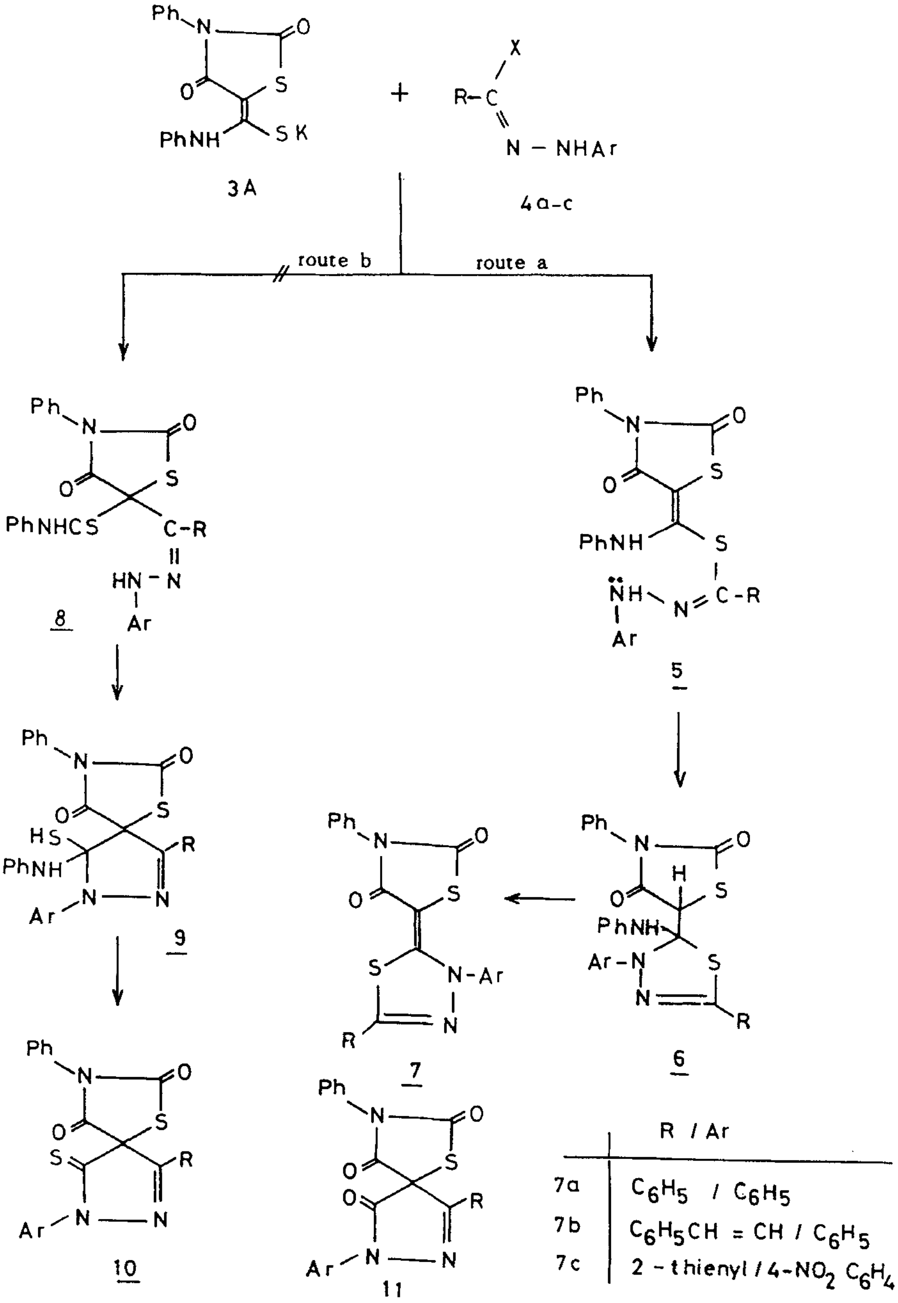
SCHEME 1

assignment was substantiated by the finding that the reactions of **4a** with either **3A** or **3B** yield one and the same product namely **7a** indicating the elimination of an arylamine molecule during the reaction.

The reaction pathway that seems to account for the formation of **7** from **3** and **4a–c** is outlined in Scheme 2. It is proposed that the reaction involves an initial nucleophilic substitution to give **5** which undergo intramolecular cyclization to yield **6** and this followed by elimination of the elements of an arylamine to afford the end product **7** with the E configuration indicated. The Z-isomer of **7** seems to suffer some steric interaction between the N-aryl group and the C=O group.

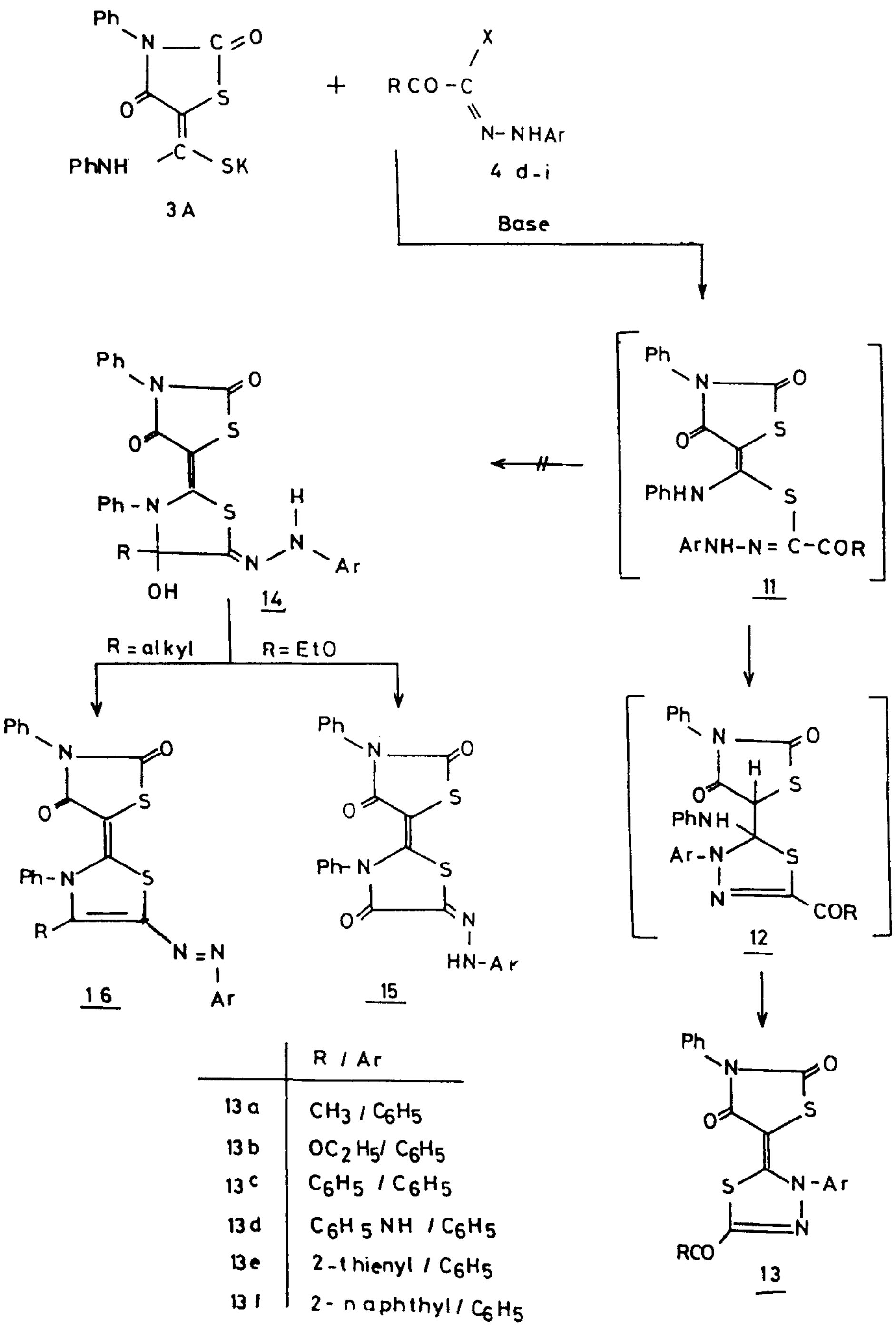
Next, the reactions of α-keto hydrazonoyl halides **4d–i** with **3A** were studied. In such cases the reaction could lead to either **13**, **15** or **16** (Scheme 3). However, when these reactions were carried out in a similar manner as that of **4a–c** with **3a**, they gave products whose spectra (IR; ^{1}H-NMR and MS) and elemental analyses were compatible with structure **13**. For example all reaction products exhibit an absorption band assignable to a carbonyl group in the region 1730–1620 cm^{-1}. The ^{1}H-NMR spectrum of the product **13** isolated from the reaction of **4** with **3A** showed the signal pattern characteristic of the ethoxycarbonyl protons, (triplet at δ 1.4 and a quartet at δ 4.4 ppm). Also, the chemical shift of the CH_3CO proton signal of the product **13a** at δ 2.7 ppm isolated from the reaction of **3A** with **4d** is similar to that observed in the ^{1}H-NMR spectrum of the starting **4d**. These data exclude both structures **15** and **16**, respectively.

The reaction course presented in Scheme 3 seems to account for the formation of **13**.



	R / Ar
7a	C_6H_5 / C_6H_5
7b	$C_6H_5CH = CH$ / C_6H_5
7c	2 - thienyl / 4-NO_2 C_6H_4

SCHEME 2



	R / Ar
13a	CH_3 / C_6H_5
13b	OC_2H_5/ C_6H_5
13c	C_6H_5 / C_6H_5
13d	C_6H_5NH / C_6H_5
13e	2-thienyl / C_6H_5
13f	2-naphthyl / C_6H_5

SCHEME 3

EXPERIMENTAL

Melting points were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra (KBr) were recorded on a Pye-Unicam SP-3000 Infrared spectrophotometer. ^{1}H-NMR spectra in $CDCl_3$ and DMSO-d_6 were recorded on a Varian EM 360 NMR spectrometer with TMS as the internal reference. Mass spectra were recorded on a GCMS-QP 1000 EX Shimadzu. Elemental analyses were carried out at the microanalytical laboratory of the University of Cairo, Giza, Egypt. The hydrazonoyl halides **4a**,[6] **4b**,[7] **4c**,[8] **4d**,[9] **4e**,[10] **4f**,[11] **4g**,[12] **4h**[13] and **4i**[14] and 2,4-thiadiazolidinedione **2**,[15] were prepared as previously described.

Preparation of 3A and 3B General method

To a stirred suspension of potassium hydroxide (0.28 g, 5 mmol) in N,N-dimethylformamide (20 ml); 3-phenyl-2,4-dioxotetrahydrothiazole (5 mmol) was added. To the resulting solution the aryl isothiocyanate (5 mmol) was added and the reaction mixture was stirred for 24 h at room temperature. The intermediates were used in solution without further separation.

Preparation of 3,5-diaryl and 3-aryl-5-aroyl-2,3-dihydro-1,3,4-thiadiazole derivatives 7 and 13 General method

A mixture of equimolar quantities of **3** in N,N-dimethylformamide and hydrazonoyl halide **4** (5 mmol each) was stirred for 30 min, then left at room temperature for **24** h. The reaction mixture was treated

TABLE I

Compd	MP. °C	Yield %	Mol. Formula	% Analysis Calcd./Found C	H	N	S
7a	294	69	$C_{23}H_{15}N_3O_2S_2$	64.3	3.5	9.8	14.9
				64.8	3.1	9.8	14.8
7b	292	63	$C_{25}H_{17}N_3O_2S_2$	65.9	3.6	8.9	13.9
				65.6	3.8	8.5	13.7
7c	190	71	$C_{21}H_{12}N_4O_4S_3$	52.5	2.5	11.7	20.0
				52.2	2.2	11.6	20.2
13a	250	65	$C_{19}H_{13}N_3O_3S_2$	57.7	3.3	10.6	16.2
				57.4	3.5	10.9	16.0
13b	256	70	$C_{20}H_{15}N_3O_4S_2$	56.5	3.5	9.9	15.1
				56.2	3.3	10.0	15.0
13c	124	78	$C_{24}H_{15}N_3O_3S_2$	63.0	3.3	9.2	14.0
				63.4	3.6	9.0	
13d	264	70	$C_{24}H_{16}N_4O_3S_2$	61.0	3.4	11.9	13.6
				61.4	3.7	11.7	
13e	312	71	$C_{22}H_{13}N_3O_3S_3$	57.0	2.8	9.1	20.7
				56.9	2.7	9.0	
13f	234	70	$C_{28}H_{17}N_3O_3S_2$	66.3	3.4	8.3	12.6
				66.2	3.1	8.0	

TABLE II

Compd	IR (cm^{-1})	^1H NMR (ppm)	MS m/z
7a	1711 (C=O), 1642 (C=O)	7.3-7.8 (m, 15H)	
7b	1669 (C=O), 1621 (C=O)	7.3-7.8 (m, 17H) 6.7 (d, 1H), 7.6 (d, 1H)	
7c	1620 (C=O)	6.6-8.2 (m, 12H)	
13a	1730 (C=O), 1646 (C=O)	2.4 (s, 3H), 7.3-7.8 (m, 10 H).	
13b	1720 (C=O), 1650 (C=O), 1640 (C=O)	1.4 (t, J = 7 Hz, 3H), 4.4 (q, J = 7 Hz, 2H); 7.3-7.7 (m, 10 H)	51, 77, 103, 135, 179, 274, 426.
13c	1714 (C=O), 1642 (C=O)	7.1-8.5 (m, 15 H)	51, 77, 105, 179, 310, 457.
13d	1685 (C=O), 1665 (C=O), 1625 (C=O)	6.8-8.2 (m; 16H)	
13e	1718 (C=O), 1685 (C=O), 1650 (C=O).	7.6-8.4 (m, 13H)	
13f	1719 (C=O), 1652 (C=O)	7.3-8.6 (m, 10 H), 9.0 (s, 7 H).	

with ethanol and the solid was collected, washed with water, dried and crystallized from N,N-dimethylformamide to give **7** and **13**, respectively (Tables I and II).

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