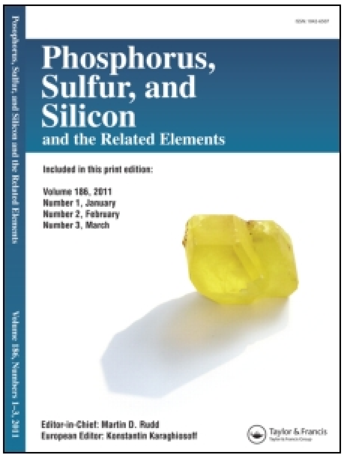

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SITE SELECTIVITY AND REGIOCHEMISTRY OF NITRILIMINES. CYCLOADDITIONS TO 1,3-DIPHENYL-2-THIONO-4-IMIDAZOLIDINONE AND ITS 5-PHENYLMETHYLENE DERIVATIVES

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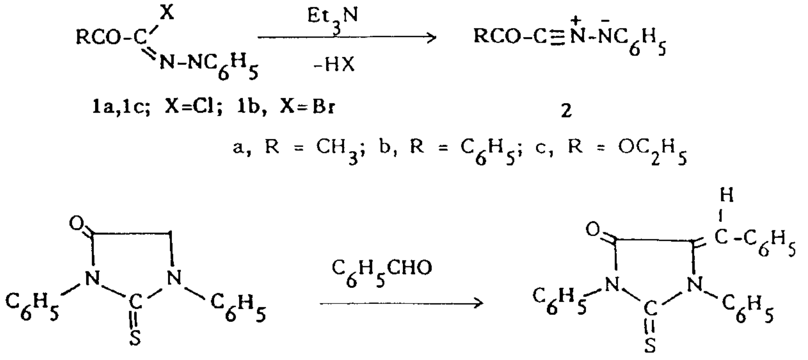
Nitrilimines **2** cycloadd to the C═S double bond of 1,3-diphenyl-2-thiono-4-imidazolidinone **3** to give the corresponding spiro compounds **5**; while their reaction with 1,3-diphenyl-5-phenylmethylene-2-thiono-4-imidazolidinone **4** lead to the formation of the spiro compounds **6** via cycloaddition to the exocyclic C═C double bond.

Key words: 1,3-Diphenyl-2-thiono-4-imidazolidinone, 1,3-diphenyl-5-phenylmethylene-2-thiono-4-imidazolidinone, hydrazonoyl halides, nitrilimines.

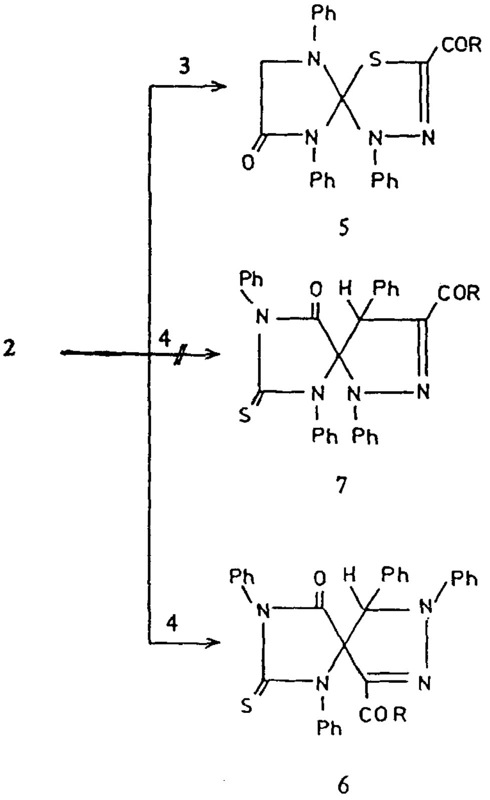
INTRODUCTION

The reactions of heterocyclic compounds with nitrilimines have been the subject of a recent review.[1] They demonstrate a useful method for the synthesis of a wide range of polyheterocycles. The results of our study of the reactions of the nitrilimines **2a–c** with 1,3-diphenyl-2-thiono-4-imidazolidinone **3** and its 5-phenylmethylene derivative **4**[2] (Scheme I) are reported here. This kind of reaction constitutes a facile route for the synthesis of novel spiro heterocyclic ring systems and is also of some site selectivity interest, as it sheds light on the competition of the C═S and C═C double bonds of **4** for the 1,3-dipoles **2a–c**.



3 4

SCHEME I



a, R = CH_3; b, R = C_6H_5; c, R = OC_2H_5

SCHEME II

RESULTS AND DISCUSSION

The nitrilimines **2**, generated in situ by the action of triethylamine on the corresponding hydrazonoyl halides **1** in chloroform, reacted readily with **3** to give the expected spiro cycloadducts **5** in good yields. To the best of our knowledge these compounds represent the first example of 4-thia-1,2,6,9-tetraazaspiro[4,4]nonan-2-ene-7-one ring system (Scheme II). The structures of such products **5a–c** were assigned on the basis of their elemental analysis and spectroscopic data (IR, ^{1}H NMR and MS), which are summarized in Tables I and II, respectively.

The reactants **4**, prepared as previously described[2] are considered to exist as the Z-isomer according to ^{1}H NMR data. Reactions of **4** with **2a–c**, as described above for **3**, gave the corresponding 2-thia-1,3,7,8-tetraazaspiro[4,4]nonan-6-ene-4-one **6a–c**, respectively (Scheme II). In no case were the other spiro cycloadducts of type **8** or **9** identified among the reaction products isolated. The structural assignment of **6** was made on the basis of their spectroscopic and elemental analysis data. In the IR spectra, they have two carbonyl absorptions in the region 1730–1680 cm^{-1}. The mass spectrum of **6a** shows a molecular ion of high intensity. In the ^{1}H NMR spectra, the pyrazoline ring proton resonates at δ 5.9–6.0 ppm. These values seem to be

TABLE I

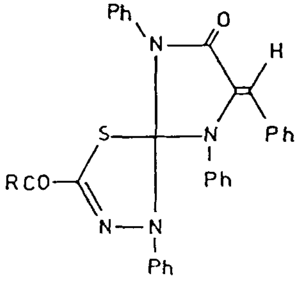
Melting points, yield, elemental analyses of the spirocycles **5a–c** and **6a–c**

Compound	Mp.	Yield %	Mol. Formula	Analysis Calcd/Found C	H	N	S
5a	195-196^{D}	75	$C_{24}H_{20}N_4O_2S$	67.3 67.0	4.7 4.9	13.1 13.0	7.5 7.4
5b	182-184^{D}	79	$C_{29}H_{22}N_4O_2S$	71.0 71.2	4.5 4.7	11.4 11.2	6.5 6.3
5c	189-190^{D}	77	$C_{25}H_{22}N_4O_3S$	65.5 65.4	4.8 4.7	12.2 12.1	7.0 7.1
6a	204-206^{E}	78	$C_{31}H_{24}N_4O_2S$	72.1 72.3	4.7 4.5	10.9 10.7	6.2 6.3
6b	93-94^{E}	75	$C_{36}H_{26}N_4O_2S$	74.7 74.9	4.5 4.2	9.7 9.4	5.5 5.6
6c	174-175^{E}	80	$C_{32}H_{26}N_4O_3S$	70.3 70.1	4.8 4.9	10.33 10.1	5.9 6.1

(D) Crystallization from N,N-dimethylformamide

(E) Crystallization from ethanol

more compatible with the regioisomeric structure **6** rather than **7** since they are very close to those reported for the 5-CH pyrazoline chemical shifts (6.0 ppm).[3] The chemical shift values of the 4-CH spiro pyrazoline derivatives **10** and **11** are 5.05–5.15 ppm and 5.20–5.30 ppm, respectively.[4,5]



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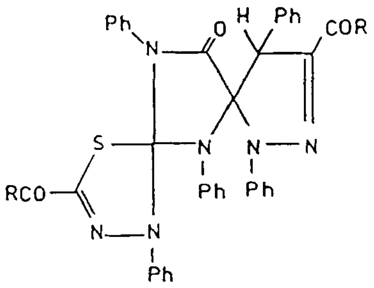

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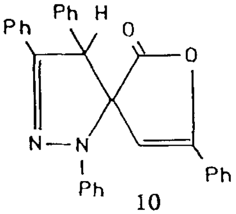

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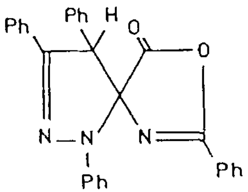

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TABLE II

IR, ^{1}H NMR and MS spectra of the spirocycles **5a–c** and **6a–c**

Compound	IR (cm^{-1})	MS	^{1}H NMR (ppm)
5a	1745, 1676	428, 320, 270, 105 77, 43	2.4 (s, 3H), 4.3 (s, 2H), 6.7-7.4 (m, 15H).
5b	1750, 1730		4.4 (s, 2H), 6.8-8.2 (m, 20H).
5c	1740, 1730	459, 350, 119 91, 51	1.3 (t, J = 7Hz, 3H), 4.2 (s, 2H), 4.3 (q, J = 7Hz, 2H) 6.6-7.5 (m, 15H).
6a	1735, 1681		2.5 (s, 3H), 5.9 (s, 1H), 7.1-7.8 (m, 20H).
6b	1730, 1720		5.9 (s, 1H), 7.1-8.0 (m, 25H).
6c	1730, 1720	546, 437, 365 324, 193, 91	1.6 (t, J = 7Hz, 3H), 4.1 (q, J = 7Hz, 2H), 5.9 (s, 1H), 7.0-7.8 (m, 20H).

The present results demonstrate that the C=S double bond, while being more reactive than the C=O double bond, is less dipolarophilic than the enone moiety of **4**. It seems that the exocyclic C=C double bond of **4** benefits from the activating and polarizing effects of the carbonyl group which determines the total control of both site selectivity and regiochemistry of the cycloaddition.

EXPERIMENTAL

Melting points were taken on a Gallenkamp apparatus and are uncorrected. Infrared spectra (KBr) were determined on a Pye Unicam SP-3000 spectrophotometer. The ^{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, Japan. Elemental analyses were carried out at the microanalytical laboratory of the University of Cairo, Giza, Egypt. 1,3-Diphenyl-2-thiono-4-imidazolidinone **3**,[2] 1,3-diphenyl-5-phenylmethylene-2-thiono-4-imidazolidinone **4**[2] and the hydrazonoyl halides **1a**,[6] **1b**[7] and **1c**[8] were prepared as previously described.

Reaction of Hydrazonoyl Halides 1 *with* 3 *and* 4

General Method: To a stirred solution of 1,3-diphenyl-2-thiono-4-imidazolidinone **3** or 1,3-diphenyl-5-phenylmethylene-2-thiono-4-imidazolidinone **4** (5 mmol) in chloroform (40 ml) was added the appropriate hydrazonoyl halide **1** (5 mmol). To the resulting mixture triethylamine (0.7 ml, 5 mmol) was added and the solution was heated at reflux for 12 h. The solvent was evaporated under reduced pressure, the residue was triturated with methanol (10 ml) and the solid was collected and crystallized from a suitable solvent to give the spiro compounds **5** or **6**, respectively. Melting points, yields, and the solvent used for crystallization are given in Table I.

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