

## Novel, Five-Membered Cyclic Betaines from the Reaction of an Ethynyl-hydrazine with Aryl Isothiocyanates

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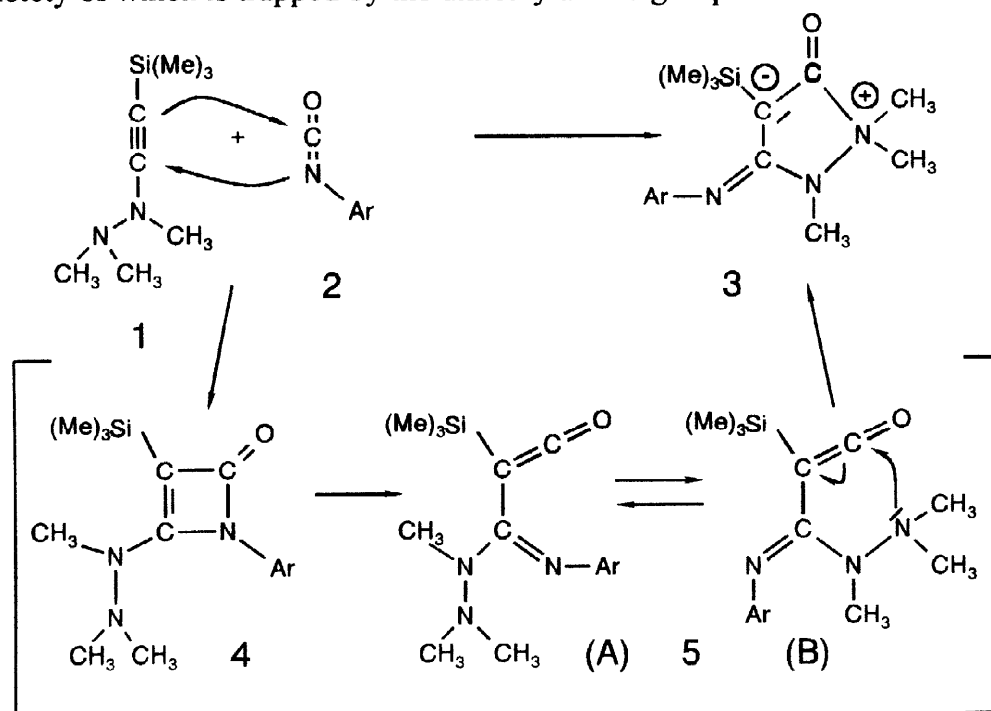
Received 10 June 1998; accepted 29 June 1998

**Abstract:** (Trimethylsilylethynyl)trimethylhydrazine **1** reacts with the aryl isothiocyanates **6** to give the corresponding 5-arylimino-1,1,2-trimethyl-4-trimethylsilyl-3-thioxo-pyrazolidinium-4-ides **7**, which can be desilylated by fluoride ion to furnish the H bearing betaines **10** (= **7**, but H instead of Me<sub>3</sub>Si). © 1998 Elsevier Science Ltd. All rights reserved.

**Keywords:** (1-alkynyl)hydrazine, cycloaddition, electrocyclic ring opening, betaines

(1-Alkynyl)amines react with *alkyl* isocyanates to furnish carbamoyl ketenimines, while with *aryl* isocyanates 4-amino-2-quinolones and/or 2-amino-4-quinolones are formed[1].

Three years ago, we examined the reactivity of the (1-alkynyl)hydrazine derivative **1** towards aryl isocyanates **2**, and we isolated five-membered cyclic betaines **3**, formed by a very specific reactivity of the ynhydrazines: the ring-opening of the firstly formed (2+2)-cycloadducts **4** between the C/C-triple bond and the C/N-double bond furnishes the amidrazono ketenes **5**, the ketene moiety of which is trapped by the dimethylamino group of the rotameric form **B**[2].

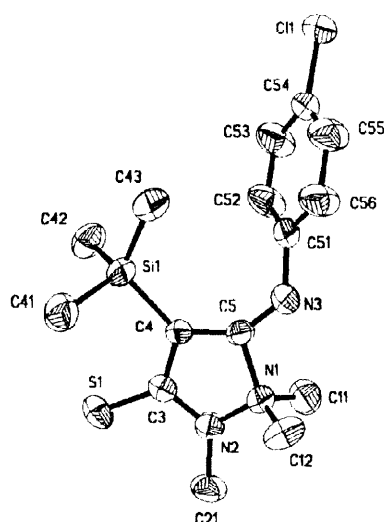


**Scheme 1.** A plausible mechanism for the reaction of the ynhydrazine **1** with aryl isocyanates and the formation of the isolated 3-arylimino-5-oxo-pyrazolidinium-4-ides **3**[2].

Now, we became interested in the question whether the ynhydrazine **1** will react with the isothiocyanates **6** in an analogous way and will furnish the corresponding betaines (**3**, but thioxo instead of the the 5-oxo group).

The reaction of the ynehydrazine **1** with the four *p*-substituted phenyl isothiocyanates **6a-d** gave in each case only one single product which proved to be 1:1 adducts[3]. Because the spectroscopic data did not elucidate their structure ( see table 1)[4], we were dependent on an X-ray investigation[5]. And this analysis of the *p*-chloro compound **7b**[5,6] clearly revealed, that 5-aryl-1,1,2-trimethyl-4-(trimethylsilyl)-3-thioxo-pyrazolidinium-4-ides **7** are formed in the reactions. The five-membered heterocycle possesses a nearly planar envelope structure. The angle between the two least square planes N2/C3/C4/C5 and N2/N1/C5 is 10.2°. The fact, that the N1-C5 bond length of 1.571(3) Å and the C4-C5-N3 angle of 144.4(2)° are relatively large, is explainable by assuming a contribution of the intermediate ketenimine **9B** to the betaine structure **7**. Zvilichkovsky called the analogous observation in the case of 2,2-dialkyl-3,5-dioxo-1,2-oxazolidinium-4-ides a contribution of an open chain „no bond resonance“ hybrid[7].

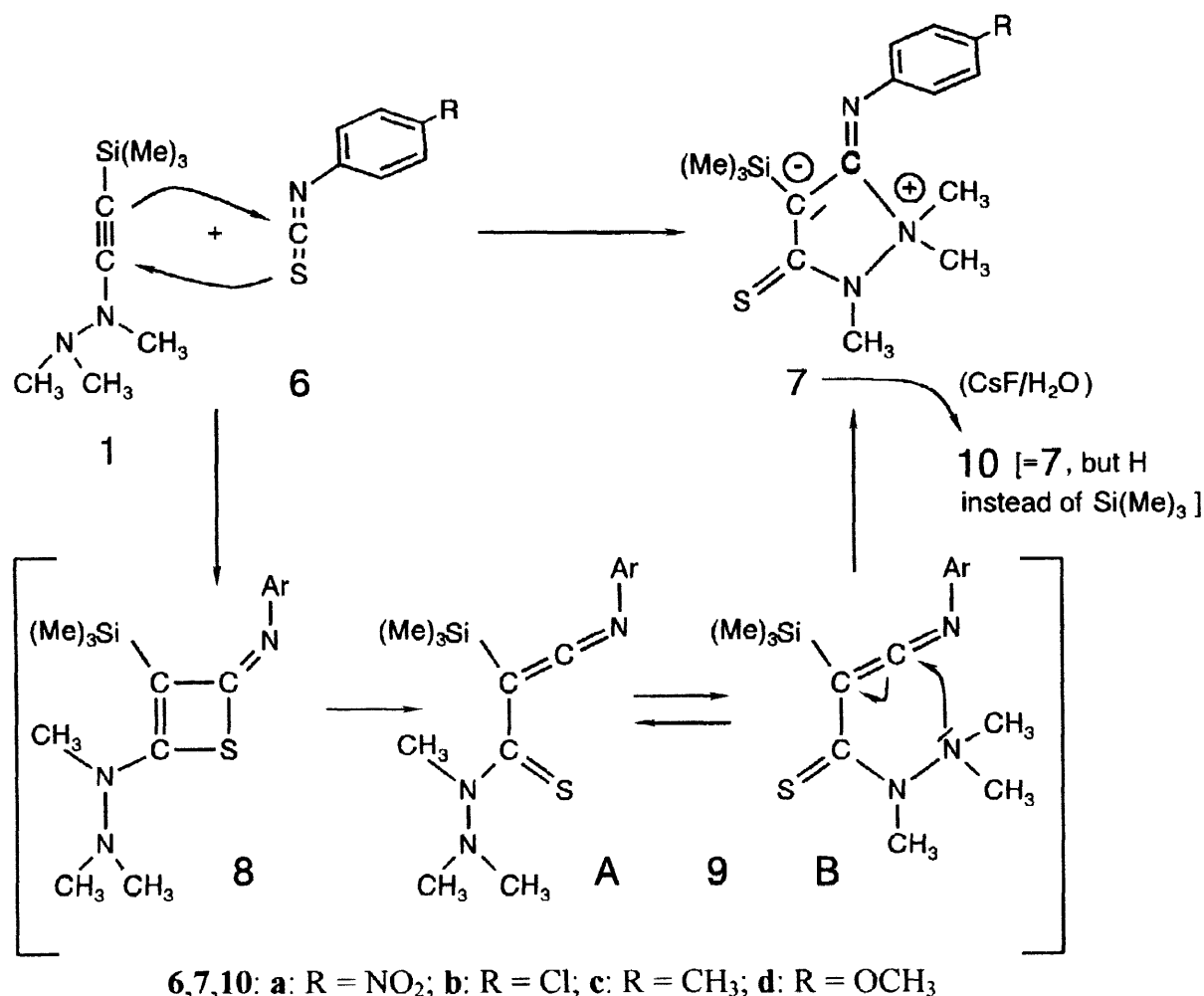
**Figure 1:** XP-Plot of **7b** ( 50% probability level), selected bond lengths (Å) and angles (°).



N1-N2	1.436(3),	N1-C5	1.571(3),
N2-C3	1.374(3),	C3-C4	1.417(3),
C4-C5	1.400(3)	C3-S1	1.679(2)
C5-N3	1.275(3),	N1-C11	1.488(3),
N1-C12	1.495(3),	N2-C21	1.436(3);
C5-N1-N2	102.9(2),	N1-N2-C3	109.8(2),
N2-C3-C4	111.4(2),	C3-C4-C5	108.1(2),
C4-C5-N1	106.5(2),	C4-C5-N3	144.4(2),
N1-C5-N3	109.0(2),	C5-N1-C11	110.6(2),
C5-N1-C12	108.7(2),	N2-N1-C11	109.7(2),
N2-N1-C12	113.2(2)	N1-N2-C21	119.4(2),
C3-N2-C21	127.6(2),	N2-C3-S1	119.0(2)
C4-C3-S1	129.5(2),	C3-C4-Si1	121.1(2),
C5-C4-Si1	130.3(2)		

The structure of our products **7** clearly reveals that here in contrast to the behaviour of aryl isocyanates **2** (see Scheme 1), the aryl *isothiocyanates* **6** do not use their C/N- but their C/S-double bond[8-10] in the starting (2+2)-cycloaddition to give the 2-imino-thietene derivatives **8**. But the remaining part of the mechanism develops analogously to that of Scheme 1: spontaneous electrocyclic ring-opening of the cycloadducts **8** furnishes the ketenimines **9**, which bear a carbothiohydrazide group, and the dimethylamino group of the rotamer **B** attacks the electrophilic carbon of the cumulenenic system to give the isolated betaines **7**.

In order to get more informative spectroscopic data, we treated our silylated five-membered cyclic betaines **7** overnight with cesium fluoride in moist acetonitrile and we isolated the hydrogen bearing compounds **10** (see Scheme 2)[11]. The <sup>1</sup>H NMR spectra show now a <sup>1</sup>H singlet at  $\delta \approx 5.4$  for the hydrogen in 4 position, while in the <sup>13</sup>C NMR spectra the concerned carbon atom causes doublets at  $\delta \approx 85.5$  with coupling constants of about 185 Hz (see Table 1).



**Scheme 2.** A plausible mechanism for the reaction of the ynehydrazine **1** with aryl isothiocyanates **6** and the formation of the isolated 5-arylimino-3-thioxo-pyrazolidinium-4-ides **7**.

**Table 1.** Spectroscopic data of the betaines **7** and **10**

	IR-KBr C=N <sup>a</sup> vs	<sup>1</sup> H NMR NMe <sub>2</sub> (s)	-CDCl <sub>3</sub> NMe(s)	<sup>b</sup> SiMe <sub>3</sub> (s)	<sup>13</sup> C NMR NMe <sub>2</sub> (q) <sup>c</sup>	-CDCl <sub>3</sub> NMe(q) <sup>d</sup>	<sup>b</sup> C-4(s)	C-5(s)	C-3(s)
<b>7a</b>	1630	3.36	3.64	0.01	50.10	30.02	86.25	168.57	197.72
<b>7b</b>	1652	2.95	3.50	0.13	46.87	30.11	76.72	169.13	196.70
<b>7c</b>	1652	2.62	3.38	0.22	44.60	29.95	68.25	168.35	196.80
<b>7d</b>	1659	2.57	3.34	0.20	44.36	29.76	67.29	167.81	196.59
				4-H (s)			C-4(d) <sup>e</sup>		
<b>10a</b>	1631	3.45	3.61	5.48	51.18	29.87	86.33	164.43	190.71
<b>10b</b>	1655	3.37	3.54	5.33	50.93	30.00	84.97	163.51	188.80
<b>10c</b>	1654	3.34	3.50	5.33	50.71	30.01	84.94	162.77	187.65
<b>10d</b>	1658	3.33	3.50	5.34	50.70	30.03	84.89	162.30	187.45

a) in cm<sup>-1</sup>; b) δ values are given; (<sup>1</sup>H- and <sup>13</sup>C-NMR); c) <sup>1</sup>J = 145.0 Hz (**7a**); 140.8 Hz (**7b**); 138.0 Hz (**7c**); 137.7 Hz (**7d**); 146.0 Hz (**10a**); 145.8 Hz (**10b**); 145.6 Hz (**10c**); 145.7 Hz (**10d**); d) <sup>1</sup>J ≈ 140 -141 Hz (**7,10a-d**); e) doublets <sup>1</sup>J = 185.4 Hz (**10a**); 184.7 Hz (**10b**); 184.6 Hz (**10c**); 184.6 Hz (**10d**)

**Acknowledgment:** Financial support by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie is gratefully acknowledged.

## REFERENCES and NOTES

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2. Gerulat, O.; Himbert, G.; Bergsträßer, U. *Synlett* **1995**, 835 - 836.
3. Products **7** were isolated as yellow or orange crystalline compounds in about 50% yield: mp: (**7a**) 137 - 8°C; (**7b**) 108 - 9°C; (**7c**) 126 - 7°C; (**7d**) 113 - 6°C.
4. The chemical shifts of the -N(Me)N(Me)<sub>2</sub>-moiety (<sup>1</sup>H- and <sup>13</sup>C-values) and their comparison with those of the isocyanate adducts **3** point out the existence of betaines, but at the very least, they do not reveal the positions of the thioxo- and of the arylimino group.
5. X-ray crystal structure analysis of **7b**: single crystals are obtained by crystallization from CHCl<sub>3</sub>. C<sub>15</sub>H<sub>22</sub>ClN<sub>3</sub>SSi, f.w. = 339.96, monoclinic, space group P2<sub>1</sub>/c, a = 6.254(1), b = 10.560(1), c = 27.125(2) Å, β = 90.04(1), V = 1791.4(4) Å<sup>3</sup>, Z = 4, ρ<sub>cal</sub> = 1.260 Mg/m<sup>3</sup>, μ = 0.394 mm<sup>-1</sup>, F(000) = 720, crystal size 0.50 x 0.40 x 0.30 mm. Data are collected on a Siemens-P4 diffractometer, MoK<sub>α</sub> radiation, 4543 reflections are measured, 3152 independent reflections (R<sub>int</sub> = 0.0175). The structure was solved by direct methods (SHELXS-86[6a]) and refined against F<sup>2</sup> (SHELXL-93[6b]). The refinement of 2466 reflections [I ≥ 2σ(I)] converge at R1 = 0.0424, wR2 = 0.1031 (all data: R1 = 0.0594, wR2 = 0.1197), GOF = 0.977, largest difference peak and hole are 0.256 and -0.246 eÅ<sup>-3</sup>. Further details of the crystal structure of compound **7b** can be obtained from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ (UK) on quoting the full journal citation.
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8. There is known in the literature, that ynamines are able to react with the C/S bond[9] and/or with the C/N bond[10] of isothiocyanates.
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11. We isolated our desilylated products (see **10**) by column chromatography in about 80% yield as yellow to orange compounds: mp: (**10a**) 123 - 4°C; (**10b**) 102 - 103°C; (**10c**) 109 - 111°C; (**10d**) 109 - 110°C.