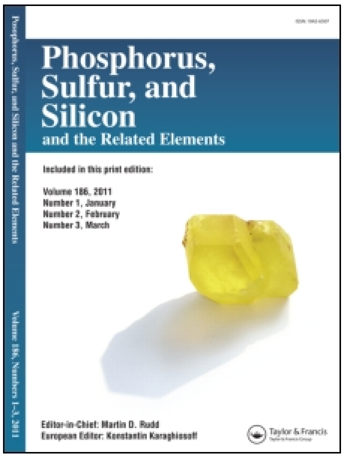

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Three-Component Condensation of 2,4-Diaminoselenazole with Aldehydes and Meldrum's Acid: Synthesis of 7-Aryl(alkyl)-Substituted 2-Amino-6,7-dihydro-4*H*-selenazolo[4,5-*b*]pyridin-5-ones

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To cite this Article Dudinov, Arkady A. , Komogortsev, Andrey N. , Lichitsky, Boris V. and Krayushkin, Mikhail M.(2010) 'Three-Component Condensation of 2,4-Diaminoselenazole with Aldehydes and Meldrum's Acid: Synthesis of 7-Aryl(alkyl)-Substituted 2-Amino-6,7-dihydro-4*H*-selenazolo[4,5-*b*]pyridin-5-ones', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 5, 1230 — 1234

To link to this Article: DOI: 10.1080/10426501003773753
URL: http://dx.doi.org/10.1080/10426501003773753

Phosphorus, Sulfur, and Silicon, 185:1230–1234, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426501003773753

THREE-COMPONENT CONDENSATION OF 2,4-DIAMINOSELENAZOLE WITH ALDEHYDES AND MELDRUM'S ACID: SYNTHESIS OF 7-ARYL(ALKYL)-SUBSTITUTED 2-AMINO-6,7-DIHYDRO-4*H*-SELENAZOLO[4,5-*b*]PYRIDIN-5-ONES

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A method for the synthesis of 7-aryl(alkyl)-substituted 2-amino-6,7-dihydro-4H-selenazolo [4,5-b]pyridin-5-ones 5 based on three-component condensation of in situ–generated 2,4-diaminoselenazole 7 with aromatic (aliphatic) aldehydes 9 and Meldrum's acid 10 was developed.

Keywords 7-Aryl(alkyl)-substituted 2-amino-6,7-dihydro-4*H*-selenazolo[4,5-*b*]pyridin-5-ones; 2,4-diaminoselenazole; Meldrum's acid; three-component condensation

INTRODUCTION

Previously, we developed a convenient method for the preparation of 7-aryl(alkyl)-substituted 2-amino-6,7-dihydro-4*H*-thiazolo[4,5-*b*]pyridin-5-ones **1** based on a three-component condensation of aromatic or aliphatic aldehydes **2**, Meldrum's acid **3**, and unstable 2,4-diaminothiazoles generated in situ from the corresponding stable 2-amino-4-iminothiazolidinium hydrochlorides **4**[1] (Scheme 1).

RESULTS AND DISCUSSION

The purpose of this study was to extend the proposed approach to the synthesis of unknown 7-aryl(alkyl)-substituted 2-amino-6,7-dihydro-4*H*-selenazolo[4,5-*b*]pyridin-5-ones **5** (Scheme 2).

4-Imino-4-aminoselenazolidine hydrochloride **6** was prepared by a known method.[2,3] It should be emphasized that the use of 2,4-diaminoselenazole **7** in a free state is almost impossible due to its low stability. In addition, diamine occurs in solution in equilibrium

Received 23 November 2008; accepted 24 November 2008.

Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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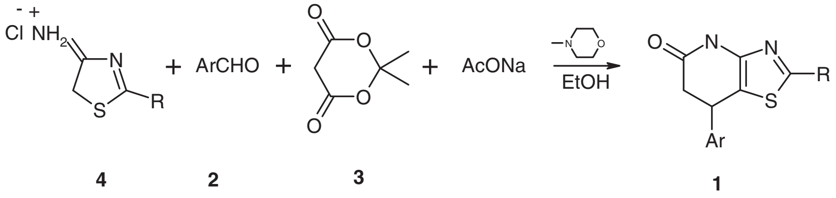
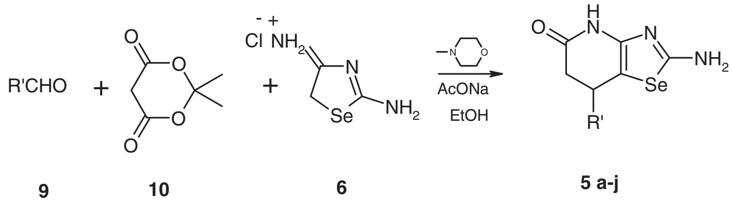


Scheme 1



R’ = 3-Cl-C_6H_4 (a); 3-F-C_6H_4 (b); 3,4-methylenedioxy-C_6H_3 (c); 4-MeO-C_6H_4 (d); 3-MeO-C_6H_4 (e); 3,4,5- $(MeO)_3C_6H_2$ (f); 3-CF_3-C_6H_4 (g); 3-OH-4-MeO-C_6H_3 (h); 4-Cl-C_6H_4 (i); $(CH_3)_2CHCH_2$ (j).

Scheme 2

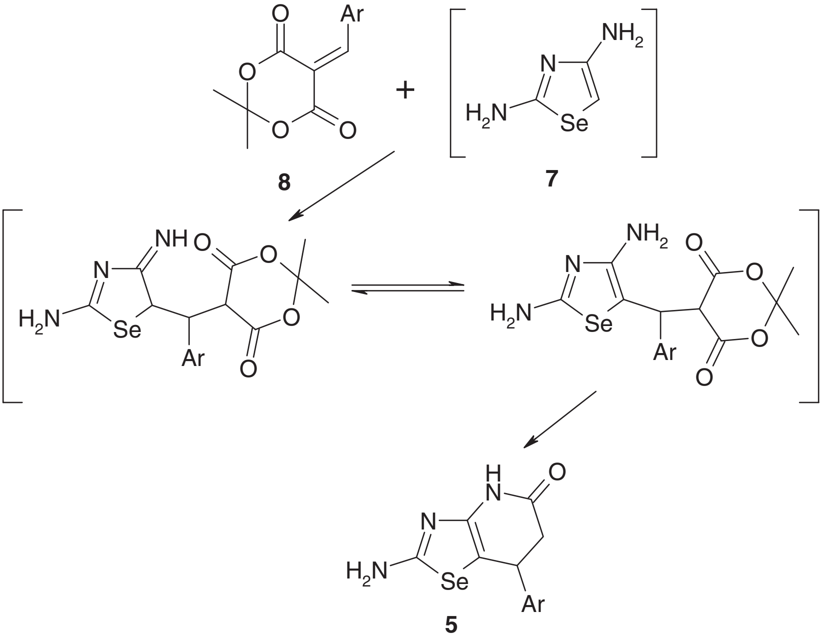
with its tautomer, 2-amino-4-iminoselenazolidine;[4] the imino form predominates and, in turn, it can be easily hydrolyzed.

The three-component condensation of compound **6** with aldehydes **2** and Meldrum’s acid **3** was carried out in refluxing ethanol in the presence of a slight excess of anhydrous sodium acetate and a catalytic amount of N-methylmorpholine. Presumably, free 2,4-diaminoselenazole **7** is formed initially in the reaction mixture under the action of sodium acetate, the process being accompanied by evolution of an equimolar amount of acetic acid and the arylmethylene Meldrum’s acid derivative **8** (from aldehyde **2** and Meldrum’s acid **3**). This is followed by conjugate Michael addition of 2,4-diaminoselenazole **7** to the arylmethylene Meldrum’s acid derivative, and subsequent cyclization of the resulting Michael adduct accompanied by CO_2 and acetone elimination (Scheme 3).

The reaction products **5** were crystalline solids; their structures were confirmed by data of IR and NMR spectroscopy, mass spectrometry, and elemental analysis (Tables I and II).

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 557 instrument (KBr). ^1H and ^{13}C NMR spectra were measured on Bruker Avance II 300 and Bruker DRX-500 instruments in DMSO-d_6. Mass spectra were run on a Finnigan MAT INCOS 50 mass spectrometer (direct injection, electron impact, 70 eV). Melting points were measured on a Boetius hot stage and were not corrected. The reactions were monitored, and the product purity was checked by TLC (Merck Silica gel 60 F254 plates, elution with ethyl acetate–hexane).



Scheme 3

Table I Melting points, yields, elemental analysis, and mass spectrometry data for compounds **5**

Compound	Mp/ °C	Yield (%)	Calculated/Found (%) C	H	N	Molecular formula MS, m$^+$/z
5a	221–223 (dec.)	73	44.13	3.09	12.86	$C_{12}H_{10}ClN_3OSe$
			44.30	3.20	12.79	327
5b	>250 (dec.)	60	46.47	3.25	13.55	$C_{12}H_{10}FN_3OSe$
			46.31	3.33	13.48	310
5c	227–229 (dec.)	68	46.44	3.30	12.50	$C_{13}H_{11}N_3O_3Se$
			46.60	3.39	12.43	336
5d	219–221 (dec.)	74	48.46	4.07	13.04	$C_{13}H_{13}N_3O_2Se$
			48.28	4.15	13.12	322
5e	217–219 (dec.)	80	48.46	4.07	13.04	$C_{13}H_{13}N_3O_2Se$
			48.30	4.14	13.11	322
5f	210–212 (dec.)	58	47.13	4.48	13.04	$C_{15}H_{17}N_3O_4Se$
			47.30	4.56	13.11	382
5g	>250 (dec.)	38	43.35	2.80	11.67	$C_{13}H_{10}F_3N_3OSe$
			43.17	2.71	11.74	360
5h	209–211 (dec.)	53	46.17	3.87	12.42	$C_{13}H_{13}N_3O_3Se$
			46.34	3.79	12.50	338
5i	221–224 (dec.)	76	44.13	3.09	12.86	$C_{12}H_{10}ClN_3OSe$
			44.30	3.18	12.93	327
5j	223–225 (dec.)	44	44.12	5.55	15.44	$C_{10}H_{15}N_3OSe$
			43.95	5.65	15.52	272

Table II IR and NMR spectroscopic data for compounds **5**

Compound	IR [KBr, cm^{-1}]	^1H NMR [δ ppm, J Hz]	^{13}C NMR [δ ppm]
5a	1668 (CONH, δ NH_2); 3184, 3308, 3392 (NH_2)	2.53 dd (1H, C^1H_2, J = 7, 16), 2.92 dd (1H, C^2H_2, J = 7, 16), 4.25 dd (1H, CH, J = 7, 7), 7.18–7.38 m (6H, C^6H_4, NH_2), 10.12 s (1H, NH)	
5b	1656 (CONH, δ NH_2); 3188, 3308, 3368 (NH_2)	2.53 dd (1H, C^1H_2, J = 7, 16), 2.90 dd (1H, C^2H_2, J = 7, 16), 4.27 dd (1H, CH, J = 7, 7), 7.05 m (2H, C^6H_2), 7.38 m (4H, C^6H_2, NH_2), 10.19 s (1H, NH)	37.48 (CH), 40.09 (CH_2, J = 7), 97.12 (C−Se), 113.47 (C_{Ar}, J = 5), 113.75 (C_{Ar}, J = 5), 122.92 (C_{Ar}, J = 3), 130.63 (C_{Ar}, J = 8), 143.75 (NH−C−N), 147.44 (C_{Ar}, J = 7), 162.29 (C−F, J = 242), 168.87 (C−NH_2), 168.98 (C=O)
5c	1664 (CONH, δ NH_2); 3064, 3180, 3404 (NH_2)	2.53 dd (1H, C^1H_2, J = 7, 16), 2.82 dd (1H, C^2H_2, J = 7, 16), 4.14 dd (1H, CH, J = 7, 7), 5.98 s (2H, OCH_2O), 6.67–6.84 m (3H, C^6H_3), 7.30 s (2H, NH_2), 10.05 s (1H, NH)	
5d	1664 (CONH, δ NH_2); 3196, 3308, 3380 (NH_2)	2.53 dd (1H, C^1H_2, J = 7, 16), 2.82 dd (1H, C^2H_2, J = 7, 16), 3.72 s (3H, OCH_3) 4.15 dd (1H, CH, J = 7, 7), 6.86 d (2H, C^6H_2, J = 8), 7.13 d (2H, C^6H_2, J = 8), 7.29 s (2H, NH_2), 10.05 s (1H, NH)	37.21 (CH), 40.34 (CH_2), 55.05 (OCH_3), 98.74 (C−Se), 113.97 (C_{Ar}), 114.13 (C_{Ar}), 127.84 ($2C_{Ar}$), 136.42 (NH−C−N), 143.24 (C_{Ar}), 158.11 (C−OCH_3), 168.69 (C−NH_2), 169.14 (C=O)
5e	1664 (CONH, δ NH_2); 3184,3292,3396 (NH_2)	2.53 dd (1H, C^1H_2, J = 7, 16), 2.85 dd (1H, C^2H_2, J = 7, 16), 3.72 s (3H, OCH_3) 4.18 dd (1H, CH, J = 7, 7), 6.79 m (3H, C^6H_3), 7.22 m (1H, C^6H_1), 7.28 s (2H, NH_2), 10.01 s (1H, NH)	
5f	1668 (CONH, δ NH_2); 3188, 3296, 3396 (NH_2)	2.62 dd (1H, C^1H_2, J = 7, 16), 2.78 dd (1H, C^2H_2, J = 7, 16), 3.64 s (3H, OCH_3), 3.73 s (6H, $2OCH_3$), 4.18 dd (1H, CH, J = 7, 7), 6.56 s (2H, C^6H_2), 7.26 m (2H, NH_2), 9.99 c (1H, NH)	
5g	1668 (CONH, δ NH_2); 3204,3320,3396 (NH_2)	2.58 dd (1H, C^1H_2, J = 6, 16), 2.95 dd (1H, C^2H_2, J = 7, 16), 4.37 dd (1H, CH, J = 6, 7), 7.31 s (2H, C^6H_2), 7.52–7.60 m (4H, C^6H_2, NH_2), 10.11 c (1H, NH)	
5h	1656 (CONH, δ NH_2); 3316, 3388, 3540 (NH_2)	2.50 dd (1H, C^1H_2, J = 7, 16), 2.81 dd (1H, C^2H_2, J = 7, 16), 3.72 s (3H, OCH_3) 4.05 dd (1H, CH, J = 7, 7), 6.59 m (2H, C^6H_2), 6.82 m (1H, C^6H_1), 7.28 c (2H, NH_2), 8.88 s (1H, OH), 10.01 c (1H, NH)	
5i	1644 (CONH, δ NH_2); 3184, 3300, 3372 (NH_2)	2.53 dd (1H, C^1H_2, J = 7, 16), 2.90 dd (1H, C^2H_2, J = 7, 16), 4.24 dd (1H, CH, J = 7, 7), 7.21 d (2H, C^6H_2, J = 8), 7.32 m (4H, C^6H_2, NH_2), 10.18 s (1H, NH)	37.22 (CH), 40.06 (CH_2), 97.32 (C−Se), 128.60 ($2C_{Ar}$), 128.75 ($2C_{Ar}$), 131.35 (NH−C−N), 143.46 (C_{Ar}), 143.66 (C−Cl), 168.90 (C−NH_2), 169.02 (C=O)
5j	1656 (CONH, δ NH_2); 3180, 3300, 3352 (NH_2)	0.85 m (6H, $2CH_3$), 1.27 m (2H, CH_2), 1.61 m (1H, CH), 2.20 dd (1H, C^1H_2, J = 7, 16), 2.59 dd (1H, C^2H_2, J = 7, 16), 2.91 dd (1H, CH, J = 7, 7), 7.26 m (2H, NH_2), 9.99 c (1H, NH)	

7-Aryl(alkyl)-2-amino-6,7-dihydro-4*H*-selenazolo[4,5-*b*]pyridin-5-ones (5): General Procedure

A mixture of 2-amino-4-iminoselenazolidine hydrochloride **2** (0.60 g, 3 mmol), Meldrum's acid (0.49 g, 3.4 mmol), anhydrous sodium acetate (0.25 g, 3.1 mmol), N-methylmorpholine (0.06 g, 0.6 mmol), and the appropriate aldehyde (3 mmol) in ethanol (8 mL) was refluxed for 4 h. The reaction mixture was cooled, and the precipitate was filtered off and washed on the filter with ethanol (3 × 5 mL) and water (3 × 5 mL).

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