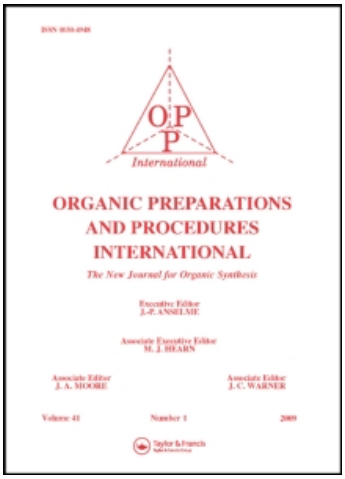


Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A FACILE SYNTHESIS OF ARYLAZOSELENAZOLES AND OF AROYLSELENADIAZOLES

Hamdi M. Hassaneen[a]; Ahmed M. Farag[a]; Mohammed S. Algharib[ab]; Ahmad S. Shawali[ac]
[a] Department of Chemistry, Faculty of Science, University of Cairo, Giza, EGYPT [b] Faculty of Engineering and Technology, Suez Canal University, Port Said, EGYPT [c] Department of Chemistry, Faculty of Science, King, Abdulaziz University, Jeddah, SAUDI ARABIA

To cite this Article Hassaneen, Hamdi M. , Farag, Ahmed M. , Algharib, Mohammed S. and Shawali, Ahmad S.(1988) 'A FACILE SYNTHESIS OF ARYLAZOSELENAZOLES AND OF AROYLSELENADIAZOLES', Organic Preparations and Procedures International, 20: 5, 505 — 510
To link to this Article: DOI: 10.1080/00304948809356296
URL: http://dx.doi.org/10.1080/00304948809356296

ORGANIC PREPARATIONS AND PROCEDURES INT. 20(5), 505-510 (1988)

A FACILE SYNTHESIS OF ARYLAZOSELENAZOLES AND OF AROYLSELENADIAZOLES

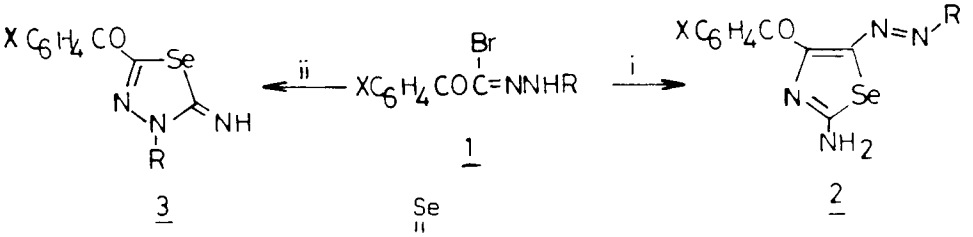
Hamdi M. Hassaneen*, Ahmed M. Farag, Mohammed S. Algharib†† and Ahmad S. Shawali*†

Department of Chemistry, Faculty of Science, University of Cairo, Giza, EGYPT

††Faculty of Engineering and Technology Suez Canal University, Port Said, EGYPT

C-Aroyl-N-arylformohydrazidoyl bromides 1 are versatile starting materials in the synthesis of various heterocyclic frameworks.[1,2] In connection with our studies on the preparation of selenium heterocycles,[3] we now report the utility of 1 in the synthesis of 5-arylazo-4-aryl-2-aminoselenazoles 2 and 2-imino-2,3-dihydro-1,3,4-selenadiazoles 3. A few examples of 2 and 3 were previously prepared by the reaction of arenediazonium chlorides with 2-phenylaminoselenazole,[4] and phenacyl selenocyanate,[5] respectively.

Treatment of 1a with selenourea in ethanol yielded a product identified as 5-phenylazo-4-phenyl-2-aminoselenazole (2a). Other bromides 1b-h reacted similarly with selenourea and gave the corresponding arylazoselenazole derivatives 2b-h respectively (Scheme 1). The structure of 2a-h were confirmed by their microanalysis, spectral data and by comparison with authentic samples prepared from 2-amino-4-phenylselenazole and the corresponding diazotized anilines. With potassium selenocyanate in ethanol at room temprature, bromides 1a-c yielded the corresponding 2-imino-2,3-dihydro-1,3,4-selenadiazoles 3a-c in 68-73 % yield, respectively (Scheme 1). The structures



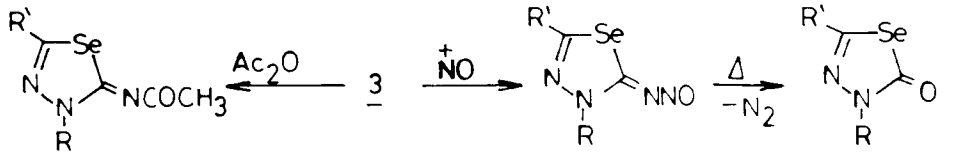
i = H_2NCNH_2 (Se) ii = KSeCN

X/R: a) H/4-$NO_2C_6H_4$ b) 4-Br/C_6H_5 c) 4-NO_2/C_6H_5

X/R: a) H/C_6H_5 b) H/4-$CH_3C_6H_4$ c) H/4-$NO_2C_6H_4$ d) H/4-BrC_6H_4 e) H/3-phenyl-5-pyrazolyl f) 4-Br/C_6H_5 g) 4-Br/4-$CH_3C_6H_4$ h) 4-Br/3-phenyl-5-pyrazolyl

Scheme 1

of 3a-c were supported by their spectra, microanalytical data and their chemical reactions outlined in Scheme 2. Thus, in the infrared spectra of 3a-c the selenocyanato absorption (2160 cm^{-1})[6] is absent. They exhibited imino NH and aroyl CO bands near 3320 and 1630 cm^{-1}, respectively (Table 1).



R' = 4-XC_6H_4CO

X/R: a) H/4-$NO_2C_6H_4$ b) 4-Br/C_6H_5 c) NO_2/C_6H_5

Scheme 2

Boiling 3 in acetic anhydride afforded the N-acetyl derivatives 4. The infrared spectra of 4 showed no NH absorption, but exhibited two carbonyl absorptions near 1640 and 1625 cm^{-1} assignable to benzoyl and N-acetylimino groups, respectively. The methyl proton resonance of the N-acetylimino

group was observed at 2.50-2.40 ppm in the ^{1}H-NMR spectra (Table 2). These spectral data and the satisfactory elemental analyses were consistent with the 2-acetylimino-3-aryl-5-aroyl-2,3-dihydro-1,3,4-selenadiazole structure 4 (Scheme 2). The treatment of 3 with sodium nitrite in acetic acid gave the N-nitrosoimino derivatives 5. The IR spectra of 5 showed no NH band, but

TABLE 1. Compounds 2a-h[a]

Compd. No.	Mp [°C]	Yield[b] [%]	IR (KBr) NH_2(cm^{-1})	NMR (DMSO-d_6) δ, ppm	Analysis % Calcd (Found) C	H	N
2a	169	68[c]	3460, 3280	7.20-8.25 (m, 10H), 8.45 (s, 2H)	55.05 (55.22)	3.70 (3.81)	17.12 (17.00)
2b	176	70	3410, 3285	3.45 (s, 3H), 7.2-8.3 (m, 9H) 8.50 (s, 2H)	56.12 (56.31)	4.13 (4.02)	16.42 (16.33)
2c	192	69	3400, 3300	7.15-8.20 (m, 9H), 8.45 (s, 2H)	48.40 (48.18)	2.98 (3.10)	18.81 (18.63)
2d	190	65	3300, 3260	7.25-8.35 (m, 9H), 8.55 (s, 2H)	44.35 (43.91)	2.73 (2.58)	13.79 (13.61)
2e	186	74[c]	3400, 3270	7.20-8.30 (m, 11H), 8.50 (s, 2H)	54.96 (55.27)	3.59 (3.78)	21.37 (21.21)
2f	203	72	3460, 3270	7.20-8.25 (m, 9H), 8.40 (s, 2H)	44.35 (44.10)	2.73 (2.61)	13.79 (13.55)
2g	206	71	3460, 3270	3.35 (s, 3H), 7.2-8.3 (m, 9H), 8.45 (s, 2H)	45.73 (45.61)	3.12 (2.98)	13.33 (13.11)
2h	226	75[c]	3410, 3110	7.20-8.3 (m, 11H), 8.45 (s, 2H)	45.78 (45.63)	2.61 (2.77)	17.80 (17.95)

a) Crystallization solvent is ethanol unless otherwise noted. b) Yield of isolated product. c) Crystallization solvent: pyridine-water.

revealed aroyl CO absorption near 1640 cm^{-1}. Boiling 5 in xylene afforded the corresponding 2-oxo-2,3-dihydro-1,3,4-selenadiazoles 6. The IR spectra of 6 showed, in each case, two carbonyl absorptions near 1640 and 1700 cm^{-1} assignable to aroyl and ring carbonyl groups respectively. Microanalytical data of 4-6 were also consistent with their assigned structure (Table 2).

TABLE 2. Compounds 3-6

Compd. No.	Mp [°C]	Yield[a] [%]	IR (KBr) (cm^{-1})	NMR (DMSO-d_6) δ (ppm)	Analysis % Calcd (Found) C	H	N
3a	209	70	3320, 1630	7.3-8.4 (m)	48.27 (48.11)	2.70 (2.66)	15.01 (15.21)
3b	145	68	3300, 1630	7.2-8.4 (m)	44.25 (44.21)	2.47 (2.52)	10.32 (10.16)
3c	199	73	3320, 1660	7.3-8.5 (m)	48.27 (48.13)	2.70 (2.81)	15.01 (15.18)
4a	171	85	1640, 1617	7.2-8.4 (m), 2.47 (s)	49.17 (49.00)	2.91 (2.86)	13.49 (13.34)
4b	175	90	1640, 1620	7.3-8.3 (m), 2.42 (s)	45.45 (45.22)	2.69 (2.51)	9.35 (9.51)
4c	185	79	1650, 1620	7.2-8.5 (m), 2.45 (s)	49.17 (49.32)	2.91 (2.83)	13.49 (13.57)
5a	148(d)	75	1630	7.3-8.4 (m)	44.79 (44.76)	2.25 (2.11)	17.41 (17.62)
5b	147(d)	70	1640	7.2-8.3 (m)	41.31 (41.12)	2.08 (2.21)	12.85 (12.77)
6a	160	80	1700, 1640	7.4-8.4 (m)	48.14 (47.93)	2.42 (2.33)	11.23 (11.39)
6b	130	75	1700, 1640	7.3-8.5 (m)	44.14 (44.30)	2.22 (2.16)	6.86 (6.66)

[a] Yield of isolated pure product.

EXPERIMENTAL SECTION

Mps were determined on a capillary apparatus and are uncorrected. The IR spectra were measured with a Pye-Unicam infrared spectrophotometer, model IMT16. ^{1}H-NMR spectra were measured in DMSO with a Varian EM-390-90 MHz spectrometer, chemical shifts are in ppm from internal TMS. Elemental analyses were performed by Microanalytical Laboratory, Cairo University, Giza, EGYPT.

2-Amino-4-aryl-5-arylazoselenazoles (2). General Procedure.- To a solution of the appropriate hydrazidoyl bromide 1 (0.005 mole) in ethanol (40 ml) was added selenourea (0.01 mole). The mixture was refluxed for 4 hrs and then filtered while hot. The filtrate was poured onto crushed ice. The colored solid that separated was collected washed with water, dried and finally

crystallized from ethanol or aqueous pyridine. The compounds prepared and their physical contants are given in Table 1.

5-Aroyl-4-aryl-2-imino-2,3-dihydro-1,3,4-selenadiazoles (3). General Procedure.- To a suspension of the appropriate hydrazidoyl bromide 1 (0.005 mole) in ethanol (50 ml) was added a solution of potassium selenocyanate (0.010 mole) in water (10 ml). The mixture was stirred for 4 hrs at room temperature. During this period, the bromide 1 went into solution and the crude 3 precipitated. The latter was collected, washed with water, dried and finally recrystallized from ethanol (Table 2).

2-N-Nitrosoimino-4-aryl-5-aroyl-2,3-dihydro-1,3,4-selenadiazoles (5).- To a solution of 3 (0.005 mole) in acetic acid (30 ml) was added a cold sodium nitrite solution (0.7 g in 10 ml water) dropwise while stirring. The mixture was left in an ice box for 6 hrs. The reddish solid that precipitated was collected. Recrystallization from dilute ethanol gave the corresponding nitroso derivative 5 (Table 2).

2-N-Acetylimino-4-aryl-5-aroyl-2,3-dihydro-1,3,4-selenadiazoles (4).- A solution of the appropriate 3 (0.005 mole) in acetic anhydride (25 ml) was refluxed for 1 h. The excess solvent was then distilled and the residue was triturated with water. The crude solid was collected, washed with water and crystallization from acetic acid gave the acetyl derivative 4 (Table 2).

5-Aroyl-4-aryl-2,3-dihydro-1,3,4-selenadiazol-2-ones (6).- The appropriate nitroso derivative 5 (1 g) was refluxed in xylene (30 ml) for 2 hrs and the solvent was then distilled under reduced pressure. The residue was triturated with little methanol. The solid, which formed, was collected and recrystallized from ethanol to give 6 (Table 2).

REFERENCES

† Present address: Department of Chemistry, Faculty of Science, King, Abdulaziz University, P. O. Box 9028, Jeddah 21413, SAUDI ARABIA.

1. A. S. Shawali and C. Párkányi, J. Heterocycl. Chem., 17, 833 (1980); A. S. Shawali, Heterocycles, 20, 2239 (1983) and references cited therein.
2. A. S. Shawali and A. O. Abdelhamid, Tetrahedron Lett., 163 (1975).
3. A. O. Abdelhamid, H. M. Hassaneen and A. S. Shawali, J. Heterocycl. Chem., 20, 719 (1983) and previous papers in the series.
4. E. Bulka and K.D. Ahlers, Z. Chem., 3, 388 (1963).
5. M. Takahashi and M. Kurosawa, Bull. Chem. Soc. Jpn., 53, 1185 (1980).
6. Y. Y. Kharitonov and V. V. Skopenko, Zh. Neorg. Khim., 10, 1803 (1965), Chem. Abstr. 64, 168 (1966).

(Received September 15, 1987; in revised form May 19, 1988)