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The Synthesis of 2-Imino-2,3-dihydro-1,3,4-selenadiazole Derivatives

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Synopsis. The reaction of phenacyl selenocyanate with arenediazonium chlorides afforded 3-aryl-5-benzoyl-2-imino-2,3-dihydro-1,3,4-selenadiazoles, which were then acetylated and nitrosated to give the corresponding 2-acetylimino and 2-nitrosoimino derivatives respectively.

As compared with the chemistry of 1,3,4-thiadiazole,[1] that of 1,3,4-selenadiazole is less known, it has been studied intensively for only the last 10 years.[2] A few 1,3,4-selenadiazole derivatives have been shown to have significant antibacterial activity.[3] Recently it has been reported by Shawali *et al.*[4] that the diazonium coupling reaction of phenacyl thiocyanate (**1**) is a convenient route to 2-imino-2,3-dihydro-1,3,4-thiadiazoles (**2**). Similarly, the reaction of 3-thiocyanatopentane-2,4-dione (**3**) led to the one-step synthesis of **2**.[5] Accordingly, it appears possible to obtain 2-imino-2,3-dihydro-1,3,4-selenodiazoles by reacting phenacyl selenocyanate (**4**) with arenediazonium chlorides. We thus obtained the expected compound from readily-available starting material, **4**, in one step, although the yields were rather low. The direct synthesis of 2,3-dihydro-1,3,4-selenadiazoles has so far been known in only one case, *i.e.*, the reaction of hydrazonyl halides with potassium selenocyanate,[6] while several derivatives have been prepared indirectly from 2-amino-1,3,4-selenadiazoles.[7]

The treatment of **4** with arenediazonium chlorides at 0—5 °C gave precipitates. These precipitates contained a significant amount of tars; attempts to obtain analytical pure samples by recrystallization were unsuccesful. Crude products which showed only one spot on a thin-layer chromatogram were, however, obtained by repeating the precipitation with ether from a hot solution of acetic acid. In the IR spectra of these crude products, the selenocyanato absorption (2160 cm^{-1}) presented in **4** disappeared, and new imino absorptions were observed in the region of 2950—2860 cm^{-1} (Table 1). Although these IR spectra suggested the cyclization to the expected 3-aryl-5-benzoyl-2-imino-2,3-dihydro-1,3,4-selenadiazoles (**5**), the structure of **5** were not confirmed ultimately until their acetylation and nitrosation, since the elemental analyses of **5** were unsatisfactory because of the difficulties in purification.

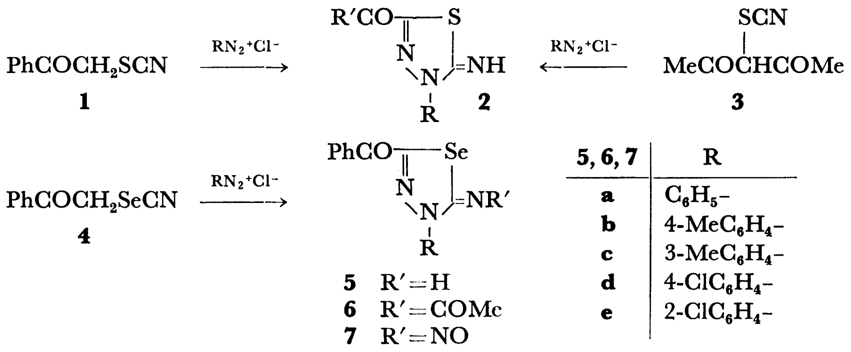
The reflux of **5** in acetic anhydride afforded the acetate (**6**) in good yields (Table 2). The IR spectra of **6** showed no NH absorption, but exhibited two carbonyl absorptions in the regions of 1650—1621 cm^{-1} and 1636—1615 cm^{-1}, which were assigned to benzoyl carbonyls and acetyl carbonyls respectively. The meth-

Table 1. Physical properties of **5**

5	Yield/%	Mp/°C	IR (KBr) ν_{max}/cm^{-1}		
a	26	199—203	2880 1592	1637 1573	1620 1530
b	53	204—210	2950 1594	1633 1575	1610 1530
c	28	174—178	2860 1593	1640 1574	1610 1523
d	28	205—211	2920 1595	1637 1574	1615 1532
e	15	204—208	2900 1576	1640 1536	1594 1477

Table 2. Physical properties and analytical data of **6** and **7**

Compound	Yield %	Mp °C	IR (KBr) ν_{max}/cm^{-1}			NMR (CDCl$_3$) δ/ppm ArH	ArMe	COMe	C% Found (Calcd)	H% Found (Calcd)
6a	89	169—171 (DMF-MeOH)	1645 1578	1615 1509	1594 1490				55.04 (55.15)	3.70 (3.54)
6b	89	153—155 (MeOH)	1632 1572	1620 1502	1592 1454	7.23—8.37(m)	2.44(s)	2.37(s)	56.38 (56.26)	4.17 (3.93)
6c	72	165—167 (DMF-MeOH)	1621 1510	1594 1485	1574 1464	7.28—8.41(m)	2.45(s)	2.38(s)	56.14 (56.26)	3.95 (3.93)
6d	61	148—150 (DMF-MeOH)	1650 1575	1636 1532	1595 1479	7.40—8.37(m)		2.39(s)	50.47 (50.45)	2.98 (2.99)
6e	65	198—201 (DMF-MeOH)	1640 1578	1633 1519	1600 1481	7.43—8.39(m)		2.30(s)	50.37 (50.45)	3.00 (2.99)
7a	80	128—129 (MeOH)	1635 1510	1590 1486	1573 1458	7.40—8.40(m)			50.46 (50.43)	2.86 (2.82)
7b	87	126—128 (MeOH)	1632 1520	1595 1504	1575 1431	7.26—8.34(m)	2.45(s)		52.00 (51.76)	3.56 (3.26)
7c	80	129—131 (DMF-MeOH)	1640 1580	1612 1525	1597 1492	7.36—8.44(m)	2.47(s)		51.94 (51.76)	3.25 (3.26)
7d	85	129—130 (MeOH)	1645 1512	1592 1484	1574 1447	7.43—8.40(m)			46.10 (46.00)	2.33 (2.32)
7e	81	125—127 (DMF-MeOH)	1645 1521	1596 1479	1577 1448	7.47—8.43(m)			46.03 (46.00)	2.13 (2.32)



5 R'=H
6 R'=COMe
7 R'=NO

5, 6, 7	R
a	C_6H_5-
b	4-MeC_6H_4-
c	3-MeC_6H_4-
d	4-ClC_6H_4-
e	2-ClC_6H_4-

yl proton resonances were observed at δ 2.30—2.39 ppm in the NMR spectra. These spectral data and the satisfactory elemental analyses were consistent with the 2-acetylimino-3-aryl-5-benzoyl-2,3-dihydro-1,3,4-selenadiazole structures (**6**).

The treatment of **5** with sodium nitrite in acetic acid at room temperature gave the nitrosoimino derivatives (**7**), red to orange, in good yields (Table 2). The IR spectra of **7** showed no NH absorption, but did display carbonyl absorptions in the region of 1645—1632 cm^{-1}. The structures of 3-aryl-5-benzoyl-2-nitrosoimino-2,3-dihydro-1,3,4-selenadiazoles (**7**) were also supported by the NMR and analytical data.

Experimental

The IR and NMR spectra were taken on a JASCO IRA-2 spectrometer and a JEOL-PMX 60 spectrometer respectively. The elemental analyses were performed on a Shimadzu UM-3B apparatus.

*Reaction of **4** with Arenediazonium Chlorides.* To a stirred and ice-cooled solution of **4**[8] (2.2 g, 10 mmol) and sodium acetate (2.5 g) in MeOH (50 ml), an aqueous arenediazonium chloride solution (19 ml) prepared from arylamine (15 mmol) in the usual manner was added, drop by drop, below 5 °C. After stirring below 5 °C for 5 h, the separated solids were collected by filtration and rinsed with ether. They were dissolved into hot acetic acid, and then the solution was poured into ether. The collection of the resulting precipitates gave, as the crude products, **5a**—**e**.

*Acetylation of **5**.* A solution of **5** (1.0 mmol) in acetic anhydride (5 ml) was refluxed for 1 h. The subsequent evaporation of the solvent, rinsing of the residue with ether, and recrystallization gave the pure acetates (**6a**—**e**).

*Nitrosation of **5**.* To a stirred solution of **5** (1.0 mmol) in acetic acid (5 ml), an aqueous solution (2 ml) of sodium nitrite (140 mg, 2.0 mmol) was added, drop by drop, at room temperature. After 1 h, a small amount of water was added to the red solution, and the precipitates thus formed were collected by filtration. The subsequent rinsing of the precipitates with water, followed by recrystallization, afforded the pure nitroso derivatives (**7a**—**e**).

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