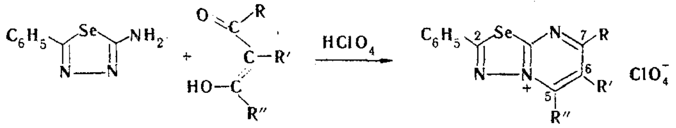
1,3,4-SELENADIAZOLO[3,2-a]PYRIMIDINIUM SALTS

V. A. Chuiguk, D. I. Sheiko,
and V. G. Glushakov

UDC 547.859'794.3

5-Amino-2-phenyl-1,3,4-selenadiazole (I) in the presence of $HClO_4$ reacts with β-diketones, β-chlorovinyl ketones, β-chlorovinyl aldehydes, β-dialdehyde acetals, and β-keto aldehydes and their acetals to give the previously unknown 1,3,4-selenadiazolo[3,2-a]pyrimidinium salts (II), which are recrystallized from CH_3COOH (IIf was recrystallized from CF_3COOH).



I

II a-f

II a $R'=H$, $R=R''=CH_3$; b $R=R'=R''=H$; c $R'=R''=H$, $R=CH_3$; d $R''=H$, $R=R'=CH_3$;

e $R=R'=H$, $R''=C_6H_5$; f $R'=R''=H$, $R=C_6H_5$

Amine I reacts with 3-chloro-2-methylbuten-2-al to give IId with an unsubstituted α position with respect to the nodal nitrogen atom, in contrast to other aminoheterocycles, which react with β-chlorovinyl aldehydes to give γ-unsubstituted substances (for example, see [1]). 1,1-Dimethoxy-3-butanone also gives one isomer (IIc), whereas phenyl β-chlorovinyl ketone gives a mixture of isomers IIe and IIf in a ratio of 1:1; these isomers were separated by recrystallization. Salts IIa,c,d are capable of forming polymethine dyes due to the activity of the methyl groups in the 5 and (or) 7 positions.

EXPERIMENTAL

5,7-Dimethyl-2-phenyl-1,3,4-selenadiazolo[3,2-a]pyrimidinium Perchlorate (IIa). A mixture of 0.92 g (0.004 mole) of amine I, 0.6 ml (0.005 mole) of 57% perchloric acid, 6 ml of ethanol, and 0.5 ml (0.005 mole) of acetylacetone was refluxed for 1.5 h. The mixture was cooled, and the resulting precipitate was removed by filtration (0.82 g) and recrystallized to give 50% of a product with mp 255-257°. PMR spectrum (in CF_3COOH, δ with respect to hexamethyldisiloxane, ppm): 2.48 (7-CH_3) 2.77 (5-CH_3), 7.33 (6-H), 7.15 (m, 3H), and 7.52 (m,2H). Salt IIb was similarly obtained from I and 1,1,3,3-tetraethoxypropane (after heating for 30 min). A product with mp 220° was obtained in 27% yield. PMR spectrum: 7.2 (m, 3H), 7.6 (m, phenyl 2H and 6-H), 8.85 (7-H, $J_1 = 4.5$, $J_2 = 1.5$ Hz), 9.28 ppm (5-H, $J_1 = 7$, $J_2 = 1.5$ Hz). Compound IIc, with mp 201-203°, was obtained in 64% yield from I and 1,1-dimethoxy-3-butanone after standing for 2 days in methanolic $HClO_4$. PMR spectrum: 2.56 (7-CH_3), 7.05 (phenyl 3H), 7.40 (phenyl 2H and 6-H), 8.88 ppm (5-H, J = 7 Hz). Compound IId, with mp 260-262°, was obtained in 45% yield by the method in [2] from I and 3-chloro-2-methylbuten-2-al. PMR spectrum: 2.22 (6-CH_3), 2.48 (7-CH_3), 7.15 (3H), 7.5 (2H), and 8.82 ppm (5-H). A mixture of IIe and IIf (1:1) was obtained in an overall yield of 30% by the method in [2] from I and phenyl β-chlorovinyl ketone. Salt IIe, with

---

T. G. Shevchenko Kiev State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1435-1436, October, 1974. Original article submitted February 18, 1974.

mp 222-223°, was eluted from the mixture with hot acetic acid. PMR spectrum: 7.2 (each 3H 2-C_6H_5 and 5-C_6H_5), 7.5 (each 2H 2-C_6H_5 and 5-C_6H_5 and 6-H), 8.68 ppm (7-H, J = 5 Hz). The residue was IIf with mp 257-258° (from CF_3COOH). PMR spectrum: 7.2 (each 3H 2-C_6H_5 and 7-C_6H_5), 7.5 (2H 2-C_6H_5 and 6-H), 7.9 (2H 7-C_6H_5), and 8.96 (5-H, J = 7 Hz). All salts II gave satisfactory analyses for Cl, while IIa,b,d gave satisfactory analyses for Cl and N.

LITERATURE CITED

1. M. K. Pordeli, V. V. Oksanin, and V. A. Chuiguk, Khim. Geterotsikl. Soedin., 1285 (1973).
2. A. N. Nesmeyanov and M. I. Rybinskaya, Dokl. Akad. Nauk SSSR, 118, 297 (1958).