4. A. C. Veronese, G. Cavicchioni, P. Giori, M. P. Quaglio, and M. Guarneri, Gazz. Chim. Ital., 106, 179 (1976).
5. M. Kruszynski and G. Kupryszewski, Roczn. Chem., 50, 1099 (1976).
6. B. O. Handford, J. H. Jones, G. T. Young, and T. F. N. Johnson, J. Chem. Soc., No. 12, 6814 (1965).
7. M. Fujino and O. Nishimura, Chem. Pharm. Bull. (Tokyo), 17, 1937 (1969).
8. P. Ya. Romanovskii, V. É. Muizhnieks, and G. I. Chipens, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 2, 227 (1971).
9. P. J. Romanovskii (Romanovski), V. E. Muizhnieks, and G. I. Chipens, Peptides 1972, Amsterdam, North-Holland (1973), p. 97.
10. P. Ya. Romanovskii, A. Yu. Krikis, I. S. Yankovska, É. É. Liepin'sh, G. I. Chipens, and G. Kupryszewski, Summaries of Papers Presented at the Third All-Union Symposium on the Chemistry of Peptides and Proteins [in Russian], Kiev (1974), p. 129.
11. T. Plucinski, P. Romanowski, and G. Kupryszewski, III Krajowa Konferencja Chemia Aminokwasow i Peptydow, Streszczenia Komunikatow, Warszawa (1975), p. 9.
12. G. Kupryszewski and M. Formela, Zeszyty Naukowe Wysz. Szkoly Pedagog. Gdansk, Mat., Fiz., Chem., 2, 131 (1962).
13. M. Bodanszky, Nature, 175, 685 (1955).
14. P. Cecchi, Ricerca Sci., 28, 2526 (1958).
15. Landolt-Boernstein, Zahlenwerte und Funktionen, Berlin, Springer-Verlag (1960), 6 Aufl., Bd. 2, 7. Teil, S. 17.
16. B. Kehl (editor), Laboratory Technique of Organic Chemistry [Russian translation], Mir, Moscow (1966), p. 591.
17. S. Ginsburg and I. B. Wilson, J. Amer. Chem. Soc., 79, 481 (1957).
18. B. Iselin and R. Schwyzer, Helv. Chim. Acta, 39, 57 (1956).

ORGANIC COMPOUNDS OF SELENIUM AND TELLURIUM

II.[*] SYNTHESIS OF BENZO[b]SELENOPHENE DERIVATIVES BY REACTION OF DIBENZAL- AND BENZALACETONE WITH SELENIUM TETRABROMIDE

V. L. Lendel, Yu. V. Migalina,
S. V. Galla, A. S. Koz'min,
and N. S. Zefirov

UDC 547.739.3

2,3-Disubstituted 2,3-dihydrobenzo[b]selenophenes were obtained in the form of trans isomers by the action of selenium tetrabromide on dibenzal- and benzalacetone in benzene.

It has been previously shown [1] that the addition of selenium tetrahalides to 1,5- and 1,6-diolefins and their derivatives is accompanied by the formation of unique products – heterocyclic compounds containing selenium in the ring. It might have been assumed that dibenzalacetone, as a 1,4-diolefin derivative, would behave like the indicated dienes in the reaction with selenium tetrabromide. However, the high selectivity of electrophilic addition could be disrupted owing to competitive substitution in the aromatic ring [2].

A study of the reaction of selenium tetrabromide with dibenzalacetone showed that the only products are benzo[b]selenophene derivatives IIa and IIIa. The structures of the isolated compounds were confirmed by IR, PMR, and UV spectral data and the results of analysis. Benzoselenophene derivatives are evidently formed

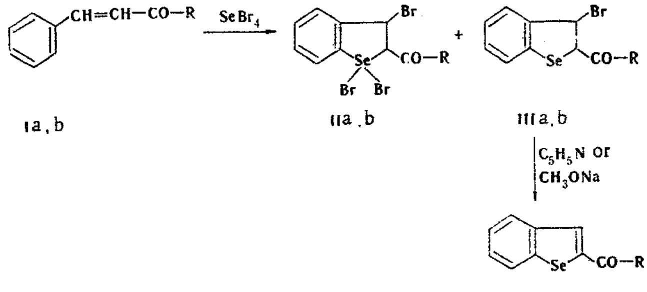
---

[*] See [1] for communication I.

Uzhgorod State University, Uzhgorod 294000. M. V. Lomonosov Moscow State University, Moscow 117234.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1340-1342, October, 1977. Original article submitted February 24, 1977.

0009-3122/77/1310-1072$07.50

in this reaction as a result of successive or simultaneous addition of selenium tetrabromide to the double bond and substitution in the ortho position of the benzene ring. In the case of an unsaturated ketone with one double bond – benzalacetone – the reaction also leads to the formation of benzoselenophenes IIb and IIIb.



I–IIIa, IV R = $C_6H_5CH=CH$; I–IIIb R = CH_3

Judging from the magnitude of the spin–spin coupling constants (11 Hz), the 2,3-disubstituted 2,3-dihydrobenzo[b]selenophenes were isolated in the form of their trans isomers. The cis isomers that are, in principle, possible could not be isolated.

The reduction of tribromo derivatives IIa and IIb with sodium sulfide by a known method [3] gives the corresponding monobromides IIIa and IIIb.

Compound IIa was also synthesized by condensation of ketone IIb with benzaldehyde. In addition, it was shown that monobromo derivative IIIa is readily dehydrobrominated under the influence of pyridine or sodium methoxide to 2-cinnamoylbenzo[b]selenophene IV. The UV spectrum of this substance contains three absorption maxima that attest to the aromatic character of the ring. Another confirmation of this is afforded by the presence in the PMR spectrum of a signal at 7.29 ppm, which is characteristic for the benzo[b]selenophene system [4].

EXPERIMENTAL

The monitoring of the course of the reactions and the evaluation of the individuality of the compounds were accomplished by thin-layer chromatography (TLC) on activity II aluminum oxide in an ether–hexane system (2 : 1). The IR spectra of mineral oil suspensions of the compounds were recorded with an IKS-22 spectrometer. The UV spectra of ethanol solutions of the compounds were recorded with an SF-4A spectrophotometer. The PMR spectra were obtained with a Tesla BS-478A-A spectrometer with tetramethylsilane as the internal standard.

1,1,3-Tribromo-2-cinnamoyl-2,3-dihydrobenzo[b]selenophene (IIa) and 3-Bromo-2-cinnamoyl-2,3-dihydrobenzo[b]selenophene (IIIa). A 16-g (0.04 mole) sample of selenium tetrabromide was added with stirring to a solution of 9.36 g (0.04 mole) of dibenzalacetone (Ia) in 150 ml of benzene, and the resulting precipitate was removed by filtration and dried in a vacuum dessiccator to give 11.55 g (52%) of IIIa with mp 167°C (from CCl_4) and R_f 0.69. IR spectrum: 1692 (C = O) and 1610-1620 cm^{-1} (CH= CH and aromatic protons). UV spectrum, λ_{max} (log ε): 225 (2.35) and 305 nm (2.61). PMR spectrum (in CCl_4): 5.25 (1H, d, J = 11 Hz, H_α), 5.52 (1H, d, J = 11 Hz, H_β), 6.94 (1H, d, J = 16 Hz, –CH=), 7.90 (1H, d, J = 16 Hz, = CH–), and a multiplet centered at 7.36 ppm (9H, aromatic). Found: C 52.1; H 3.3; Br 20.6%. $C_{17}H_{13}BrOSe$. Calculated: C 52.0; H 3.3; Br 20.4%.

Workup of the benzene layer after drying with calcium chloride yielded 4.1 g (26%) of IIa with mp 214°C (from $CHCl_3$–CCl_4, 1 : 1) and R_f 0.75. IR spectrum: 1692 (C = O) and 1610-1620 cm^{-1} (CH= CH and aromatic protons). UV spectrum, λ_{max} (log ε): 225 (2.64) and 306 nm (3.02). PMR spectrum (in $CDCl_3$): 5.32 (1H, d, J = 11 Hz, H_α), 5.54 (1H, d, J = 11 Hz, H_β), 6.86 (1H, d, J = 16 Hz, –CH=), 7.77 (1H, d, J = 16 Hz, = CH–), and a multiplet centered at 7.35 ppm (9H, aromatic). Found: C 36.6; H 2.3; Br 43.4%. $C_{17}H_{13}Br_3OSe$. Calculated: C 37.0; H 2.4; Br 43.7%. The same substance was obtained in 56% yield by heating IIIb (see below for its preparation) and benzaldehyde in the presence of traces of potassium hydroxide. The samples of IIa obtained by the different methods were identical with respect to their IR spectra and R_f values, and no melting-point depression was observed for a mixture of the two products.

Reduction of tribromo derivative IIa with sodium sulfide gave a monobromide identical to IIIa obtained by the method described above with respect to their IR and UV spectra and chromatographic mobilities. No melting-point depression was observed for a mixture of the two products.

2-Cinnamoylbenzo[b]selenophene (IV). A) A 1.6-g (0.02 mole) sample of pyridine was added with stirring to a solution of 1.9 g (0.005 mole) of IIIa in 100 ml of benzene, and the resulting solution was refluxed for 48 h. The precipitated pyridine hydrobromide was removed by filtration, the benzene was vacuum evaporated from the filtrate, and the residual oil was dissolved in dry benzene. The benzene solution was saturated with dry hydrogen chloride, and the precipitate was removed by filtration. Evaporation of the filtrate gave 1.4 g (90.3%) of anhydrous crystals with mp 86-87°C and R_f 0.69. UV spectrum, λ_{max} (log ε): 250 (3.63), 265 (3.69), and 310 nm (4.11). PMR spectrum ($CDCl_3$): 4.93 (1H, d, J = 10 Hz, $-CH=$), 5.38 (1H, d, J = 10 Hz, $=CH-$), 7.29 (1H, s, H_β), and a multiplet centered at 7.38 ppm (9H, aromatic). Found: C 65.5; H 3.7%. $C_{17}H_{12}OSe$. Calculated: C 65.6; H 3.9%.

B) Treatment of monobromide IIIa with sodium methoxide gave IVa (in 90% yield) which was identical to the substance obtained by method A with respect to their R_f values and UV and IR spectra.

1,1,3-Tribromo-2-acetyl-2,3-dihydrobenzo[b]selenophene (IIb) and 3-Bromo-2-acetyl-2,3-dihydrobenzo-[b]selenophene (IIIb). A 39.9-g (0.1 mole) sample of selenium tetrabromide was added with stirring to a solution of 14.6 g (0.1 mole) of benzalacetone in 250 ml of benzene, and the resulting precipitate was removed by filtration and dried in a vacuum desiccator to give 11 g (36%) of IIIb with mp 86°C (from $CHCl_3$) and R_f 0.65. IR spectrum: 1692 cm^{-1} (C=O). Found: C 58.5; H 4.1; Br 27.0%. $C_{10}H_{10}BrOSe$. Calculated: C 58.8; H 4.1; Br 26.6%.

Workup of the benzene solution after drying with calcium chloride gave 16.4 g (35%) of IIb with mp 121°C (from CCl_4) and R_f 0.82. IR spectrum: 1692 cm^{-1} (C=O). PMR spectrum (CCl_4): 2.4 (3H, s, CH_3), 4.75 (1H, d, J = 11 Hz, H_α), 5.20 (1H, d, J = 11 Hz, H_β), and a multiplet centered at 7.32 ppm (4H, aromatic). Found: C 32.6; H 2.8; Br 51.4%. $C_{10}H_{10}Br_3OSe$. Calculated: C 33.0; H 2.8; Br 51.8%.

Reduction of tribromo derivative IIb with sodium sulfide gave monobromide IIIb (in 81% yield), which was identical with respect to its IR spectrum and R_f value to a sample of IIIb obtained by the method described above. No melting-point depression was observed for a mixture of the two samples.

LITERATURE CITED

1. Yu. V. Migalina, V. I. Staninets, V. G. Lendel, I. M. Balog, V. A. Palyulin, A. S. Koz'min, and N. S. Zefirov, Khim. Geterotsikl. Soedin., No. 1, 58 (1977).
2. R. E. Nelson, E. F. Dedering, and J. A. Bilderback, J. Am. Chem. Soc., 60, 1239 (1938).
3. E. A. Braye, W. Hübel, and J. Caplier, J. Am. Chem. Soc., 83, 4406 (1961).
4. N. N. Magdesieva, V. A. Vdovin, and N. M. Sergeev, Khim. Geterotsikl. Soedin., No. 10, 1382 (1971).