Nonclassical Selenoloselenophens

By SALO GRONOWITZ* and ANDREAS KONAR

(*Division of Organic Chemistry* 1, *Chemical Center, University of Lund, P.O. Box* 740, S-220 07 *Lund, Sweden*)

Summary Evidence for the existence of nonclassical selenoloselenophens, the 4,6-dimethyl- and 4,6 diethoxycarbonylselenolo[3,4-*c*]selenophens (**1b**) and (**1c**), which appear to be more stable than the corresponding thieno[3,4-*c*]thiophens, has been obtained.

WE report some results concerning syntheses of the first derivatives of the selenolo[3,4-*c*]selenophene system (**1**) for which the only uncharged resonance contributors are structures containing tetracovalent selenium in one of the rings. Derivatives of the corresponding sulphur-containing system, thieno[3,4-*c*]thiophen, were earlier reported by Cava *et al.*[1]

Chloromethylation of 2,5-dimethylselenophen[2] gave (89%) yellow needles of (**2a**), m.p. 71·5—73 °C. The Hinsberg reaction of dimethyl selenodiacetate and biacetyl followed by esterification of the acid and bromination with *N*-bromosuccinimide afforded in 34% overall yield yellow needles of (**2b**), m.p. 147—148 °C. Both (**2a**) and (**2b**) were cyclized with ethanolic sodium hydrogen selenide to give mixtures of (**3a**) and (**4a**), and of (**3b**) and (**4b**). Separation was achieved by steam distillation to give colourless prisms of (**3a**) (45%, m.p. 87—88 °C) and yellow needles of (**3b**) (88%, m.p. 111—113 °C).

Periodate oxidation[3] of (**3a**) and (**3b**) gave the selenoxides (**5a**) (86%, m.p. 97—99 °C) and (**5b**), and bromination with bromine in carbon tetrachloride[4] gave the dibromides (**5c**) (94%, m.p. 118—120 °C) and (**5d**) (92%, m.p. 149—151 °C).† Compound (**5a**) decomposed on the attempted crystallization from benzene, and when its solution in acetic anhydride was heated to reflux under nitrogen, an intense red-violet fluorescent colour developed

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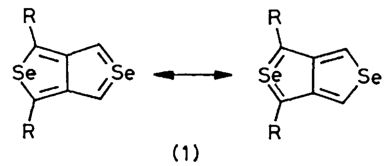
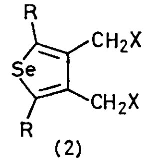
† Satisfactory elemental analyses have been obtained for compounds (**2a**), (**2b**), (**3a**), (**3b**), (**4a**), (**4b**), (**5a**), (**5c**), and (**5d**).



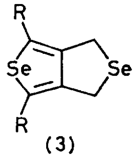
(1)

a, R = H
b, R = Me
c, R = CO_2Et



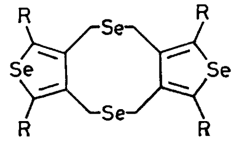
(2)

a, R = Me; X = Cl
b, R = CO_2Me; X = Br



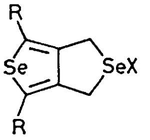
(3)

a, R = Me
b, R = CO_2Et



(4)

a, R = Me
b; R = CO_2Et



(5)

a, R = Me; X = O
b, R = CO_2Et; X = O
c, R = Me; X = Br_2
d, R = CO_2Et; X = Br_2

rapidly. This colour, which we attribute to the selenoloselenophen (**1b**), remained unchanged after an additional 3 h of refluxing. We could not, however, isolate this violet product, owing to its sensitivity to air, but in a similar dehydration in the presence of *N*-phenylmaleimide (NPM), where the violet colour disappeared after 1 h, we were able to trap the selenoloselenophen (**1b**) as its NPM adduct.

Compound (**5b**) could not be isolated in the pure state, as the extraction of its colourless methanol–water solution with any water-immiscible organic solvent gave the deep violet fluorescence of the organic-phase extracts. This colour, which we attribute to the selenoloselenophen (**1c**), developed fastest when benzene was used as a solvent and remained unchanged during 5 h. When a solution of NPM in benzene was added, the violet colour disappeared within 5 min and a few crystals of the NPM adduct precipitated. The compositions of both adducts were confirmed by their mass spectra.

When the extraction of the selenoxide (**5b**) solution was carried out with n-hexane, a u.v. spectrum of the violet hexane solution showed λ_{max} 563 nm. Extraction with C_6D_6 allowed us to record the n.m.r. spectrum of the violet benzene solution, which showed a single peak at δ 10·04 (aromatic H), which disappeared after 0·5 h.

The dibromides (**5c**) and (**5d**) were decomposed within a few minutes when stirred with 40% NaOH at 0 °C under nitrogen. When the resulting milky emulsions were stirred with hexane, (**1b**) and (**1c**) respectively, were slowly released into the organic phase (much faster when stirred with benzene); this process was followed by the appearance of a deep violet colour remaining for > 2 h in the case of (**1b**) and 5 h with (**1c**), indicating that the selenolo[3,4-*c*]-selenophen derivative substituted by electron-withdrawing groups is more stable than that substituted by electron-donating groups.

Upon attempted isolation of (**1b**) and (**1c**) in the pure state, the selenides (**3a**) and (**3b**) along with some polymeric materials were obtained. The violet colour disappeared in both cases during 5—10 min when an NPM solution in benzene was added, giving the same NPM adduct as described above. Our preliminary results also indicate that nonclassical selenoloselenophen compounds might be more stable than the corresponding sulphur ones,[1] which is somewhat unexpected considering the results obtained with selenabenzenes.[5]

(*Received, 6th December* 1976; *Com.* 1324.)

[1] M. P. Cava and M. V. Lakshmikantham, *Accounts Chem. Res.*, 1975, **8**, 139.
[2] C. Paal, *Ber.*, 1885, **18**, 2255.
[3] M. Cinquini, S. Colonna, and R. Giovini, *Chem. and Ind.*, 1969, 1737.
[4] L. E. Saris and M. P. Cava, *J. Amer. Chem. Soc.*, 1976, **98**, 867.
[5] J. Stackhouse, G. H. Senkler, Jr., B. E. Maryanoff, and K. Mislow, *J. Amer. Chem. Soc.*, 1974, **96**, 7836.