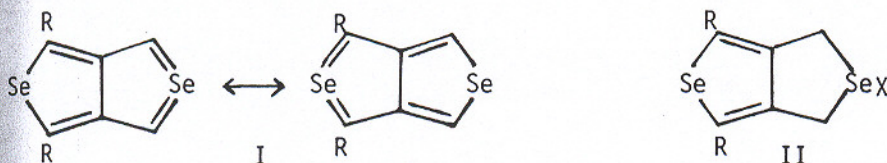


NONCLASSICAL SELENOLOSELENOPHENES

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We have recently¹ obtained evidence for the transient existence of the two derivatives Ib and Ic of the nonclassical selenolo[3,4-c]selenophene (Ia). These were formed as intermediates in both acid- and base-catalyzed dehydration of the corresponding selenoxides IIa and IIb, as well as in dehydrobromination of the dibromides IIc and IId.



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|---------------------------|----------------------------------|---|
| a. R = H | a. X = O; R = Me | d. X = Br ₂ ; R = Me |
| b. R = Me | b. X = O; R = CO ₂ Et | e. X = Br ₂ ; R = CO ₂ Et |
| c. R = CO ₂ Et | c. X = O; R = Ph | f. X = Br ₂ ; R = Ph |
| d. R = Ph | | |

In order to stabilize the nonclassical system I, we introduced phenyl substituents in positions 1 and 3 (cf. Id, IIc and IId), and then also in positions 1, 3, 4 and 6 via ring-closure reactions of suitable 1,4-diketones with phosphorus pentaselenide. Phosphorus pentaselenide was prepared by a slight modification of the method of Zingaro et al.² in which red, amorphous selenium was used instead of the grey form. This rendered the reagent

sufficiently reactive towards 1,4-diketones to effect their cyclization in moderate yields, for which reason the reaction can now be considered as a more general route to 2,5-disubstituted selenophenes than previously realized. Cycloaddition reactions of nonclassical selenoloselenophenes and thienoselenophenes will be discussed.

References:

1. S. Gronowitz and A. Konar, J. Chem. Soc. Chem. Commun. 1977, 163.
2. M.V. Kudchadker, R.A. Zingaro and K.J. Irgolic, Can. J. Chem. 1968, 46, 1415.

