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PREPARATION AND PROPERTIES OF SELENIUM IMIDES.

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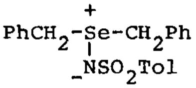
Tricoordinate tetravalent sulfonium ylides, sulfonium imides and sulfoxides are isoelectronic to each other around the central sulfur atoms and their chemical and physical properties have been extensively investigated during the past 10 years.[2] Meanwhile, among the corresponding selenium analogs the selenoxide and the selenium ylide have been synthesized and their physical and chemical features have been partly characterized, the former being reported for the first time in 1896,[3] while the latter being prepared very recently.[4] However, the synthesis of the corresponding nitrogen analogs, selenium imides, has never been attempted so far, despite of their inherently interesting nature.

In this communication we wish to report the syntheses and an interesting chemical behavior of a few selenium imides.

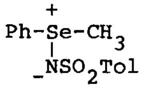
An equimolar mixture of dibenzyl selenide and tert-butyl hypochlorite was treated in CH_3CN at -30°C with an equimolar amount of solid N-sodio-p-toluenesulfonamide. After 2 hr the reaction was found to be complete as the sodium salt of the sulfonamide disappeared completely. The filtration of the precipitated sodium chloride and then the removal of the solvent from the filtrate afforded nearly quantitatively white crystals which were recrystallized from benzene-n-hexane (mp. 118-120°C). Based on the elemental analysis, nmr, and ir spectra, the structure of the material are assigned to have the following formula (I); IR, 1245(SO_2), 1120(SO_2), 1080, 950, 690 cm^{-1}. NMR, δ 2.35(s 3H), 4.28(s 4H), 7.30(s,q 14H). Found: C, 58.90; H, 4.65;

N, 3.29%. Calcd for $C_{21}H_{21}NO_2SSe$: C, 58.60; H, 4.91; N, 3.25%.

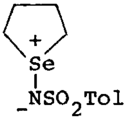


$PhCH_2-\overset{+}{Se}(-\bar{N}SO_2Tol)-CH_2Ph$ (I)

Likewise, methyl phenyl and tetramethylene selenonium N-p-toluenesulfonimides (II; mp. 129-130°C, III; mp. 125-127°C)[5] could be synthesized in almost quantitative yields. The selenium imide thus obtained was found to display an

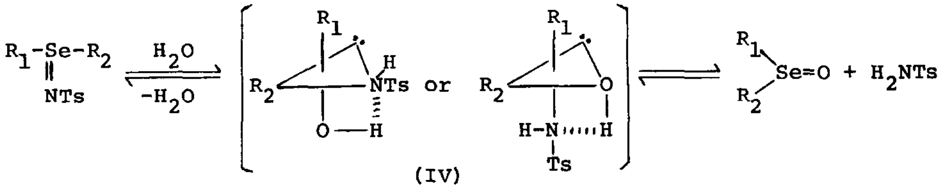


$Ph-\overset{+}{Se}(-\bar{N}SO_2Tol)-CH_3$ (II)



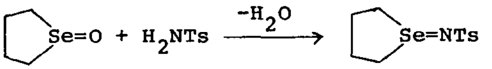
(III)

interesting chemical behavior; when I was dissolved in $CDCl_3$ saturated with a trace of water the intensities of nmr spectral peaks due to I decreased gradually, while those of the selenoxide and sulfonamide increased. Additionally, the ir spectrum of the same solution showed the increasing intensities of SO_2 unsymmetrical stretching bands at 1305 and 1325 cm^{-1}. The former was assigned that of the sulfonamide, while the latter could be attributable to that of the hydrated selenium imide (IV). The I itself was quantitatively recovered from the solution simply by evaporating the solvent. Therefore, these findings implicitly indicates that in the presence of a trace of water there is a rapid selenium imide-selenoxide equilibration proceeding through a relatively stable hydrated intermediate.



(IV)

Based on this observation, desired aliphatic selenium imides could be synthesized readily and quantitatively by dissolving a equimolar mixture of the corresponding selenoxide and sulfonamide in $CHCl_3$ and then removing the solvent and drying under vacuum. This is a most promising and

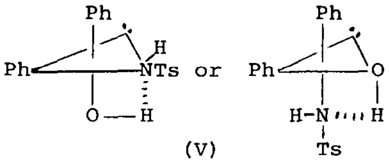


(quantitatively)

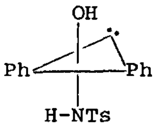
$$(PhCH_2)_2Se=O + H_2NTs \xrightarrow{-H_2O} (PhCH_2)_2Se=NTs \text{ (quantitatively)}$$

convenient method for the preparation of aliphatic selenium imides from the corresponding selenoxides.

Meanwhile, we have attempted the preparation of the corresponding selenium imide of diaryl selenide. Based on the elemental analysis and the spectroscopic data, however, the structure of the product, recrystallized from benzene-n-hexane (33.4% yields, mp. 98-99°C) as white needles, was assigned rather unequivocally as a hydrated selenium imide (V)[6] rather than the selenium imide itself; the unusually lower O-H stretching frequency of 2900 cm^{-1} strongly indicates that an intramoleculaly hydrogen-bonded structure (V) is favored over an alternative possibility (VI) which satisfies the electronegativity rule.[7] To our knowledge the isolation of such a unsymmetrical



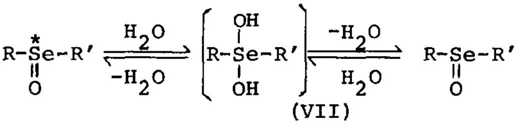
(V)



(VI)

selenium analog of tetracoordinate sulfurane containing nitrogen and oxygen as ligands has never been reported.

The fact that the semipolar Se-N bond is apt to receive the hydration would not contradict the failure to isolate the optical active selenoxide, since it is doomed that the optical activity is lost during the synthesis probably by the mechanism taking place via the hydrated intermediate (VII).[8]



$$\text{R-}\underset{\underset{\displaystyle \text{O}}{\|}}{\overset{*}{\text{Se}}}\text{-R}' \underset{-H_2O}{\overset{H_2O}{\rightleftharpoons}} \left[\text{R-}\underset{\text{OH}}{\overset{\text{OH}}{\text{Se}}}\text{-R}'\right] \underset{H_2O}{\overset{-H_2O}{\rightleftharpoons}} \text{R-}\underset{\underset{\displaystyle \text{O}}{\|}}{\text{Se}}\text{-R}'$$

(VII)

Studies on the physical properties and chemical behaviors of the selenium imides are now in progress in our laboratories.

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5. All new compounds indicated have proper analyses and spectra.
6. IR (KBr), 3300 (NH), 2900 (OH), 1330 (SO_2), 1150 (SO_2) cm^{-1}. NMR ($CDCl_3$), δ 2.40 (s 3H), 5.75 (broad,s 2H), 7.20-7.90 (m 14H). Found: C, 54.46; H, 4.52; N, 3.37%. Calcd for $C_{19}H_{19}NO_3SSe$: C, 54.29; H, 4.56; N, 3.33%.
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