Tetrahedron Letters No.34, pp. 3003-3008, 1965. Pergamon Press Ltd.
Printed in Great Britain.

# ALKYL ISOSELENOCYANATES AND RELATED COMPOUNDS

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(Received 6 July 1965)

Alkyl isoselenocyanates, R-NCSe, have been little studied and, with a single exception, have been obtained only as uncharacterised crude materials. In particular, $CH_3NCSe$ has not been reported in any form. Renson, et al. [1,2(a)] prepared ethyl[1], n-propyl, n-butyl, n-amyl and n-hexyl isoselenocyanates[2(a)] by the addition of selenium to the corresponding isonitriles in chloroform solution. They attempted to purify only the butyl compound which was obtained as a colourless liquid by distillation at a very low pressure. It discoloured rapidly under normal pressure and at room temperature and was characterised only by a qualitative infrared spectrum[2(b)]. The studies of Pedersen[3] are similar to those of Renson, et. al. and the work of Lippe, et.al.[4] and Warner[5] attests the formation of various alkyl isoselenocyanates as intermediates in certain reactions.

In this communication the preparation and isolation in pure form of $CH_3NCSe$, $C_2H_5NCSe$, n-$C_3H_7NCSe$ and iso-$C_3H_7NCSe$ is reported. N moles of the appropriate isonitrile (where N is usually 0.25) is dissolved in 5N litres of redistilled petroleum ether (40-60°) and refluxed for 4 days with 1.25 to 1.5 N moles of finely divided black selenium. A further 0.5 N moles of selenium are added and the refluxing continued for several more days. Passage of dry nitrogen through the mixture ensures steady reflux but does not prevent the formation of an amber colour. The use of precipitated red selenium appears to confer no advantage. At the end of the reaction period, unreacted selenium is filtered off, washed, dried and weighed as a check on the expected yield. The filtrate is distilled on a steam bath with the passage of a vigorous stream of nitrogen until the volume is reduced to approximately 100 ml. The remaining liquid is then removed by evaporation at room temperature in a draught of nitrogen.

In the case of $CH_3NCSe$ a brown solid is obtained while the higher homologues form dark coloured oils. The $CH_3NCSe$ is freed of the last traces of solvent and unreacted isonitrile under vacuum and is then purified by sublimation in a closed system at 2mm Hg pressure and 40-50°C. The final product is collected as white crystals on a cold finger (m.p. 68°C. Found: C,19.9; H,2.47; N, 11.8; Se, 65.5. Calc. for $C_2H_3NSe$: C,20.0; H,2.51; N,11.7; Se 65.8). The molecular weight (cryoscopic method in benzene) found for the compound, namely 120±2, agrees well with the formula weight.

The ethyl and the two propyl compounds are purified by removal of solvent and isonitrile at room temperature under vacuum and they are then distilled into a trap cooled in liquid nitrogen under a pressure of 0.05-0.10 mm Hg. Only sufficient warmth is applied to the crude material to offset evaporative cooling and as a result the temperature does not rise above room temperature. It was found that the ethyl compound was also a solid (m.p.25°C. Found: C,27.4; H, 3.9; N,10.1; Se, 58.5. Calc. for $C_3H_5NSe$: C,26.9; H,3.8; N,10.5; Se,59.0). The sample analysed had been twice distilled and the molecular weight (cryoscopic) obtained was 135±3.

In the case of the ethyl and propyl isoselenocyanates the yield is normally 70-80% but with the methyl compound yields have varied from as low as 5% up to 23%. The reason for this is not, as yet, clear: however, low yields are always associated with the recovery of a disproportionately large amount of solid material before concentration, not all of which is unreacted selenium.

All four compounds have a characteristic sharp and irritating odour and are lachrymatory. The methyl compound causes a burn on sensitive areas of the skin. They are all reduced by Zn/H Cl to the corresponding amines, identified by infrared spectroscopy. They react immediately with aqueous $AgNO_3$ solution depositing black $Ag_2Se$ and rapidly blacken metals such as Cu and Ag. They react only slowly with water but rapidly deposit red selenium when treated with aqueous acids, weak or strong. They do not appear to be light sensitive but decompose on heating. Their stability at room temperature is a function of purity and there is some evidence that the process of decomposition is auto-catalytic. The two solids may be kept at room temperature in convential glass containers for several days without change but the two propyl isoselenocyanates which are liquids and are less pure develop a yellow colour over several hours. All samples may be stored indefinitely at dry-ice temperatures.

The isonitriles required were made by the method of Jackson and McKusick[6] with the exception of $CH_3NC$. For this compound an improved procedure has been devised which is based upon the work of Hartley[7]. In this, 100g of AgCN were placed in a well stoppered flask with 230 gm of $CH_3I$ and the whole held in a thermostat at 40°C for 4 days. The brown crystalline product was filtered off, washed thoroughly with acetone, air dried and distilled under a pressure of 40 mm Hg and at 220°C into a receiver immersed in a dry ice-acetone bath. The crude yield at this point was 55%. The product was then distilled at atmospheric pressure (B.P. 59-60°C) and subsequently found to be better than 99% pure by gas chromatography.

Two other methods of preparing alkyl isoselenocyanates have been investigated. The work of Warner[5] suggested that alkyl isoselenocyanates might be obtained from N-alkyl diselenocarbamates according to the scheme:-

$$\mathrm{KOH + CSe_2 + RNH_2 \rightarrow (R - NH - CSe_2)K + H_2O}$$

$$\mathrm{2\,(R - NH - CSe_2)K + Pb(OAc)_2 \rightarrow (R - NH - CSe_2)_2Pb + 2K(OAc)}$$

$$\mathrm{(R - NH - CSe_2)_2Pb \overset{\Delta}{} 2\,RNCSe + Pb\,Se + H_2\,Se}$$

A solution of $CSe_2$ in dioxan was added to an aqueous solution of $CH_3NH_2$ and KOH with the necessary precautions[5]. The deep red-brown solution which resulted was treated with $Pb(OAc)_2$ and a bulky black precipitate formed immediately. Steam distillation of the mixture after the addition of chloroform gave an organic phase which in turn yielded a small amount of $CH_3NCSe$ on evaporation of the chloroform. The success of the isonitrile method made it unnecessary to pursue this reaction further but it is thought that it could also be developed into a suitable preparative method.

The fact that $SiH_3NCSe$ is obtained by the reaction of $SiH_3I$ with Ag Se CN[8] and $CH_3$ NC and $CH_3$ NCO by the action of $CH_3I$ on Ag CN and Ag OCN respectively, led us to investigate the action of $CH_3I$ on Ag Se CN. It was found, however, that in this case the product formed exclusively was $CH_3SeCN$.

It is of interest to note that, with the recent discovery of preparative methods for the alkyl cyanates and the work reported here, compounds of the type RXCN and RNCX (R = alkyl; X = O,S,Se) are all now available for study. We attempted to prepare $CH_3NCTe$ by reacting $CH_3NC$ with tellurium in petroleum ether but the tellurium was quantitatively recovered. This result and the similar inference of Lippe, et. al.[4], together with the work of Greenwood, et. al.[9] on the Te $CN^-$ ion suggests that stable tellurium analogues of the compounds above, do not exist.

Our primary purpose has been connected with the structure and properties of selenocyanates and isoselenocyanates and a full study of the vibrational spectra of these compounds will be published shortly. The selenocyanates are prepared by the reaction of KSeCN with alkyl iodides and bromides. The first member, $CH_3SeCN$ has been obtained quite colourless after fractionation and we have found (G.L.C.) that the colour is due to the presence of $(CH_3)_2Se_2$. As a class, the compounds are fairly stable and darken only slowly over a period of several months. The propyl compounds have not, we believe, been previously described and because of the general paucity of information the following boiling points are recorded: $CH_3SeCN$, 57°C (15 mm); $C_2H_5SeCN$, 45°C (8 mm); n-$C_3H_7SeCN$, 43°C (3 mm); iso - $C_3H_7SeCN$, 43°C (6 mm); n-$C_4H_9SeCN$, 44°C (0.6 mm). Isomerisation of selenocyanates to isoselenocyanates occurs in certain special cases [3,10] but does not appear to afford a general preparative method for the latter.

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