

hour the compound became sticky and the colour became a more intense red. M.p. 78–79°C (decomp.). (Found: C 20.45; H 3.60. Calc. for $C_4H_9PSe_2$: C 19.53; H 3.69).

The triethylphosphine compound (II) was obtained in a similar way as a green, crystalline powder, which melted at 72–75°C to a red liquid. It is soluble in most organic solvents with a green colour (it is more soluble than the corresponding carbon disulfide compound). (Found: C 29.90; H 5.37. Calc. for $C_7H_{15}PSe_2$: C 29.18; H 5.25).

On addition of tripropylphosphine to carbon diselenide in ether a green solution was first formed, but the colour soon became brown and on addition of pentane a semi-solid brown-red precipitate separated. On standing for about a week in a refrigerator the precipitate became crystalline and after stirring with a little chloroform and filtering it was isolated as a dark red crystalline powder. On heating it began to darken at 120°C and melted with decomposition at 130–132°C. (Found: C 19.2; H 2.69. Calc. for $(C_3H_7)_3P \cdot 4CSe_2$: C 18.6; H 2.50).

On adding tripropylphosphine to a solution of carbon diselenide in pentane we succeeded in isolating a green crystalline compound with the composition $(C_3H_7)_3P \cdot CSe_2$ (III). (Found: C 36.35; H 6.38. Calc.: C 36.38; H 6.41). It rapidly became red and sticky and no definite melting point could be determined. In some experiments this transformation took place before the precipitate could be filtered.

Carbon diselenide was prepared from methylene chloride and selenium¹. We thank stud.scient. J. Borchsenius Carlsen for assistance in preparing the carbon diselenide.

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Infra-red Spectra of Dithiocarboxylates and Diselenocarboxylates

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Additional evidence for the localization of the infra-red bands due to the dithio- and diselenocarboxylate ions, $-CS_2^-$ and $-CSe_2^-$ (*cf.* the preceding papers) has been found by comparison of the infra-red spectra of potassium ethylxanthate (potassium *O*-ethylthiocarbonate, $C_2H_5O-CS-SK$) and the corresponding diselenoxanthate¹ (potassium *O*-ethyldiselenocarbonate, $C_2H_5O-CSe-SeK$). The infra-red spectra of these two compounds are practically identical, apart from a strong band at 1055 cm^{-1} , found only in the spectrum of the sulfur compound, and a strong band at 942 cm^{-1} , found only in the spectrum of the selenium compound. It seems therefore rather convincing that these two bands should be ascribed to the groups $-CS_2^-$ and $-CSe_2^-$, respectively.

A comparison of the infra-red spectra of the carboxymethyl esters of ethylxanthogenic acid ($C_2H_5-CS-SCH_2COOH$) and the corresponding selenium compound ($C_2H_5O-CSe-SeCH_2COOH$) similarly served to localize the bands due to the groupings $-S-SR$ and $-Se-SeR$, respectively. Here again a strong band at 1050 cm^{-1} is only found in the spectrum of the sulfur compound, and a strong band at 950 cm^{-1} is only found in the spectrum of the selenium compound. Otherwise the spectra are almost identical.

Finally, the infra-red spectrum of zinc *N,N*-dimethyldiselenocarbamate², $[(CH_3)_2N-CSe-Se]_2Zn$ has a strong band at 878 cm^{-1} corresponding to a strong band at 981 cm^{-1} in the spectrum of zinc *N,N*-dimethyl dithiocarbamate.

Apart from diselenoxanthates and diselenocarbamates, diselenocarboxylates have hitherto been unknown. We have made several attempts to prepare esters of diseleno- or thioseleno-acids by the same methods which were used to prepare esters of dithio-acids³, but in most cases without success. It was, however, found that zinc salts of diseleno-acids are formed from dialkyl- or diarylzincs and carbon diselenide. Whereas, *e.g.*, diethylzinc is almost

unreactive towards carbon dioxide, it reacts slowly with carbon disulfide and very rapidly with carbon diselenide with formation of the zinc salts of dithiopropionic and diselenopropionic acid, respectively. Some representative diseleno-acids and their esters have been prepared in this way. Furthermore we have prepared some diselenocarboxylates from carbon diselenide and compounds with a reactive methylene group.

In the infra-red spectra of most dithiocarboxylates (salts and esters) a strong band is found near 1000–1100 cm^{-1} . A comparison of these spectra with the spectra of the corresponding selenium compounds shows that this band must actually be due to the $-\text{CS}_2^-$ or $-\text{CSSR}$ groups. The corresponding band in the spectra of the selenium compounds is found near 900 cm^{-1} .

The details of this investigation will be published in a forthcoming paper in this journal.

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Infra-red Spectra of Thioamides Selenoamides

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In connexion with other studies of thioacids and their derivatives we have also studied the infra-red spectra of a great number (about 300) of these compounds. Although this study was made mainly for practical purposes, *i.e.* to obtain useful diagnostic information, it also led to information on the controversial problem of the origin of the absorption bands in the spectra of thioamides (including thioureas,

thiohydrazides and thiosemicarbazides). Thus, we have been able to locate various characteristic bands in the spectra of these compounds of which each behaves in a characteristic way when the compounds are deuterated, S-alkylated or transformed into metal complexes. Although it may be extremely difficult to decide from which molecular vibrations these bands originate, it is often easy to localize corresponding bands in various thioamide-compounds.

As a new method we have used the comparison of corresponding sulfur and selenium compounds. The pronounced chemical similarity between sulfur and selenium is also borne out in the infra-red spectra of such compounds. Whereas the infra-red spectra of corresponding oxygen and sulfur compounds are rather different, so that an identification of a specific vibration by comparison between the spectra of sulfur and oxygen compounds may be very uncertain, the spectra of analogous sulfur and selenium compounds are almost identical, except for the bands due to the sulfur- and selenium-containing groups. This method has been used to localize dithiocarboxylate and diselenocarboxylate bands (see the preceding papers) and also to determine the P=S and P=Se absorptions in phosphine sulfides and phosphine selenides and the corresponding bands in arsine sulfides and arsine selenides.

When this method was applied to the study of thioamides, thiosemicarbazides and thioureas it was found that the spectra of the corresponding selenoamides, seleno-semicarbazides and selenoureas were virtually identical with the spectra of the thio-compounds between 1000 cm^{-1} and 3000 cm^{-1} . Thus the absorption bands of corresponding thio- and seleno-compounds appear at the same place within a few cm^{-1} and in most cases with comparable intensity. Since a vibration which appears in the spectrum of a selenium compound can obviously not be due to C=S vibration the unavoidable conclusion seems to be that thioamides do not show a C=S vibration and that all assignments of infra-red bands to this vibration — in so far as the thioamides are concerned — have been erroneous. Perhaps this is a somewhat academic remark since it is now generally agreed that most strong bands in the infra-red spectra of these compounds contain contributions from several vibrations. Nevertheless, the proponents of the latter view also assume that the bands of thioamides contain contributions from a C=S vibra-