440. *Reaction of Organomercury Compounds with Covalent Selenocyanates*

By E. E. AYNSLEY, N. N. GREENWOOD, and M. J. SPRAGUE

Selenium selenocyanate reacts with diphenyl- and dimethyl-mercury to give the compounds RHgSeCN and RSeCN (R = Ph or Me), and selenium. The new compounds phenyl- and methyl-mercury(II) selenocyanate have also been prepared by metathesis of mercury(II) selenocyanate and diphenyl-(or dimethyl-)mercury. Selenium dicyanide cleaves the phenyl–mercury bond to give phenyl selenocyanate and phenylmercury(II) cyanide. The infrared and Raman spectra of phenyl- and methyl-selenocyanate, and the infrared spectra of the compounds phenylmercury(II) selenocyanate, phenylmercury(II) cyanide, phenylmercury(II) iodide, mercury(II) selenocyanate, and methylmercury(II) selenocyanate, have been recorded and assignments made.

ALTHOUGH selenium selenocyanate, $Se(SeCN)_2$, can be prepared by a variety of routes[1] the chemistry of this compound has received little attention. However it is known that triphenylbismuth reacts with selenium selenocyanate to yield diphenylbismuth selenocyanate, phenyl selenocyanate, and selenium.[2]

$$Ph_3Bi + Se(SeCN)_2 = Ph_2BiSeCN + PhSeCN + Se$$

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[1] E. E. Aynsley, N. N. Greenwood, and M. J. Sprague, *J.*, 1964, 704.

[2] F. Challenger, A. T. Peters, and J. Halevy, *J.*, 1926, 1648.

We have found that selenocyanation in this way is also applicable to organomercury compounds. Thus, diphenylmercury reacts rapidly with selenium selenocyanate in boiling benzene to give white crystals of phenylmercury(II) selenocyanate in 85% yield, according to the equation:

$$Ph_2Hg + Se(SeCN)_2 = PhHgSeCN + PhSeCN + Se$$

By contrast, the corresponding reaction between selenium selenocyanate and dimethylmercury under similar experimental conditions proceeds slowly and methylmercury(II) selenocyanate is obtained as white crystals in only 43% yield.

$$Me_2Hg + Se(SeCN)_2 = MeHgSeCN + MeSeCN + Se$$

Both phenyl- and methyl-mercury(II) selenocyanate are photosensitive, insoluble in water, and are thermally unstable, the phenyl compound decomposing rapidly at 100° and the methyl compound at 60°. In addition methylmercury(II) selenocyanate darkens slowly on exposure to air.

Challenger[2] allowed selenium dicyanide to react with triphenylbismuth and was able to identify only phenyl selenocyanate in the products. We find that the analogous reaction between selenium dicyanide and diphenylmercury proceeds slowly in benzene solution at room temperature to give phenylmercury(II) cyanide and phenyl selenocyanate in 80—90% yield.

$$Ph_2Hg + Se(CN)_2 = PhHgCN + PhSeCN$$

Phenyl selenocyanate (m. p. —0·5°), methyl selenocyanate (m. p. —7°), and the new compounds phenylmercury(II) selenocyanate and methylmercury(II) selenocyanate have been identified by chemical analysis and infrared spectroscopy. Phenylmercury(II) cyanide (m. p. 209·5°) was identified by comparison with an authentic sample. Phenylmercury(II) selenocyanate and methylmercury(II) selenocyanate were also prepared by the metathesis reactions indicated in the equations below:

$$Ph_2Hg + Hg(SeCN)_2 = 2PhHgSeCN$$
$$Me_2Hg + Hg(SeCN)_2 = 2MeHgSeCN$$

The infrared and Raman spectra of phenyl selenocyanate and methyl selenocyanate are reported here for the first time and are compared with the infrared data for phenylmercury(II) selenocyanate and methylmercury(II) selenocyanate. The photosensitive nature of the two latter compounds precluded Raman studies.

VIBRATIONAL SPECTRA

Methyl Selenocyanate.—The infrared and Raman spectra of methyl selenocyanate, together with suggested assignments, are given in Table 1. Methyl selenocyanate has C_s symmetry with 15 fundamental modes of vibration, all of which are active in both the infrared and Raman. These normal modes consist of ten in-plane vibrations of symmetry A', and five out-of-plane, A'', vibrations. Eight modes are associated with the methyl group, namely, three C–H stretches, three CH_3 deformations, and two CH_3 rocking modes. The six vibrations involving the C–Se–C≡N framework consist of two Se–C stretches, one C≡N stretch, one Se–C_2 in-plane bend, and an in-plane and an out-of-plane Se–C≡N bend. The remaining fundamental is a torsional mode, provided that there is not free rotation of the methyl group about the rest of the molecule.

The bands observed above 900 cm.$^{-1}$ in the spectrum of methyl selenocyanate are readily assignable by comparison with published data for methyl thiocyanate.[3-5] The bands at 519 and 576 cm.$^{-1}$ can reasonably be assigned to Se–C stretching vibrations.[1,6] Comparison with the spectra of methylmercury(II) selenocyanate and phenyl selenocyanate (see below) suggests that the 519 cm.$^{-1}$ band is due to the Se–C(N) vibration, and thus the 576 cm.$^{-1}$ band corresponds to the $(H_3)C$–Se mode.

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[3] N. S. Ham and J. B. Willis, *Spectrochim. Acta*, 1960, **16**, 279.
[4] F. A. Miller and W. B. White, *Z. Elektrochem.*, 1960, **64**, 701.
[5] R. P. Hirschmann, R. N. Kniseley, and V. A. Fassel, *Spectrochim. Acta*, 1964, **20**, 809.
[6] G. Bergson, *Arkiv Kemi*, 1958, **13**, 11.

TABLE 1

The infrared and Raman spectra of methyl selenocyanate

Infrared ν (cm.$^{-1}$)	Raman ν (cm.$^{-1}$) $\varepsilon_{\text{rel.}}$	Assignment
3040w	3037 (2) dep.	Asym. C–H stretch
2946m	2946 (8) pol.	Sym. C–H stretch
2822w	2821 (1/10)	2 × 1421 = 2842. Enhanced by Fermi resonance with 2946
2670w		519 + 2153 = 2672
2549w		2 × 1279 = 2558
2510w		358 + 2153 = 2511
2340w		1421 + 932 = 2353
2153s	2152 (10) pol.	C≡N stretch
	1847 (1/15)	2 × 927 = 1854
1623w		358 + 1279 = 1637
1421ms	1423 (1/2) dep.	Asym. CH_3 deform.
	1372 (1/30)	Impurity?
1279ms	1279 (1/2) pol.	Sym. CH_3 deform.
1088w		519 + 576 = 1095
932ms	927 (1/20)	In-plane CH_3 rock
918sh,ms		Out-of-plane CH_3 rock
576w	579 (5) pol.	Se–C(H_3) stretch
519ms	520 (1) pol.	Se–C(N) stretch
393w	384 (1/10)	In-plane Se–C≡N bend
358s	365 (1/10)	Out-of-plane Se–C≡N bend
	168 (1) pol.	Se–C_2 bend

The bending mode, ν_2, in the selenocyanate ion is observed [7] at *ca.* 420 cm.$^{-1}$. Therefore the bands at 358 and 393 cm.$^{-1}$ in the infrared are assigned to the two Se–C≡N bending vibrations and comparison with the spectra of various alkyl thiocyanates [4,5] suggests that the higher-frequency band represents the in-plane bend and the lower one the out-of-plane mode.

It is probable that the methyl group does not rotate freely and that a torsional mode will occur in the region of 100 cm.$^{-1}$. However, assignment of the low-frequency band at 168 cm.$^{-1}$ to the Se–C_2 in-plane bending mode is preferred, in agreement with its observed polarisation.

Methylmercury(II) *Selenocyanate.*—The methylmercury(II) selenocyanate molecule with C_s symmetry has 18 fundamentals, all active in both the infrared and Raman. There are 12 in-plane (A') and six out-of-plane (A'') modes. The modes associated with the C–Hg–Se–C≡N framework are a C≡N, a C–Se, an Hg–Se, and an Hg–C stretch, an in-plane and an out-of-plane Se–C≡N bend, an in-plane and an out-of-plane C–Hg–Se bend, and one in-plane Hg–Se–C bend. The remaining nine fundamentals consist of a torsional mode and the methyl vibrations described above.

The infrared spectrum of methylmercury(II) selenocyanate is shown in Table 2, together with suggested group assignments. The assignments follow directly from those of methyl

TABLE 2

The infrared spectrum of methylmercury(II) selenocyanate *

ν (cm.$^{-1}$)	Assignment
2999w	Asym. C–H stretch
2915ms	Sym. C–H stretch
2786w	2 × 1403 = 2806 enhanced by Fermi Resonance with 2915
2658w	2140 + 527 = 2667
2140s	C≡N stretch
1403m	Asym. CH_3 deform.
1177m	Symmetric CH_3 deform. splitting due to crystal field?
1164s	
780s	CH_3 rock
540s	Hg–C and Se–C stretches
536s	
527s	
395w	In-plane Se–C≡N bend
374m	Out-of-plane Se–C≡N bend

* The compound was examined as a mull with Nujol or hexachlorobutadiene except in the 2400—2000 cm.$^{-1}$ region when a solution in benzene was used to remove crystal-field splitting of the 2140 cm.$^{-1}$ band.

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[7] N. N. Greenwood, R. Little, and M. J. Sprague, *J.*, 1964, 1292.

selenocyanate and the only complication in the spectrum is provided by the three bands in the 500—550 cm.$^{-1}$ region. Only two vibrations are expected to lie in this region of the spectrum, namely the Se–C and Hg–C stretching modes, and it is therefore suggested that the two bands at 536 and 540 cm.$^{-1}$ represent a single vibration split into a doublet by crystal effects. Mercury(II) selenocyanate shows an Se–C stretch at 539 cm.$^{-1}$, whilst in dimethylmercury, Hg–C stretching vibrations are observed [8] at 515 and 550 cm.$^{-1}$. Thus, the three bands observed in the spectrum of methylmercury(II) selenocyanate at 527, 536, and 540 cm.$^{-1}$ are assigned to Hg–C and Se–C stretching vibrations; a more specific assignment is not possible with the present information.

Phenyl Selenocyanate.—The infrared and Raman frequencies of phenyl selenocyanate, together with a complete assignment by the notation of Randle and Whiffen,[9] are given in Table 3.

TABLE 3

The infrared and Raman spectra of phenyl selenocyanate

Infrared ν (cm.$^{-1}$)	Raman ν (cm.$^{-1}$) $\varepsilon_{rel.}$	Assignment
3155w	3158 (1)	C–H stretches
3075sh,m		
3063m	3064 (10)	
3022sh,w	3026 (1/6)	
3000w	3004 (1/3)	
2154s	2156 (10) pol.	C≡N stretch
1954w		Phenyl combination bands
1880w		
1799w		
1740w		
1577s	1578 (3) dep.	C–C stretches k and l
1478s	1477 (1/8)	C–C stretch m
1441s	1442 (1/6)	C–C stretch n
1385w		2 × 688 = 1376
1329m		C–C stretch o
1304m		614 + 688 = 1302?
1274w		614 + 668 = 1282?
1243vw		In-plane C–H deform. e
1180w	1183 (1/2) pol.	In-plane C–H deform. a
1158w	1163 (1) dep.	In-plane C–H deform. c
1095w		477 + 614 = 1091 or 349 + 739 = 1088?
1067s	1069 (1) pol.	Substituent sensitive vibn. q, and in-plane C–H deform. d
1021s	1022 (3) pol.	In-plane C–H deform. b
1000s	1002 (7) pol.	In-plane ring deform. p
987w		Out-of-plane C–H deform. h
967w		Out-of-plane C–H deform. j
911w		Out-of-plane C–H deform. i
840w	836 (1/8)	Out-of-plane C–H deform. g
739vs		Out-of-plane C–H deform. f
688s		Out-of-plane ring deform. v
670sh,m	667 (1)	Substituent sensitive vibration r
668s		
614w	613 (1) dep.?	In-plane ring deform s
523ms	522 (1) pol.	Se–C(N) stretch
477ms	478 (1/8)	Substituent-sensitive vibration y
460sh,m		
390w	387 (1/10)	In-plane Se–C≡N bend
349s	354 (1/10)	Out-of-plane Se–C≡N bend
294s	299 (3) pol.	Substituent sensitive vibration t
239m	242 (1) dep.	Substituent-sensitive vibration u
Out of observable range	184 (1)	Substituent-sensitive vibration x

The phenyl selenocyanate molecule with probable symmetry C_s, has 36 normal modes of vibration, active in both the infrared and Raman. Thirty vibrations are associated with the phenyl group and the remaining six consist of a C≡N stretch and a Se–C stretch, an in-plane and an out-of-plane Se–C≡N bend, a C–Se–C bend, and a torsional mode.

Most of the bands in the spectra of phenyl selenocyanate due to vibrations of the phenyl

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[8] H. S. Gutowsky, *J. Chem. Phys.*, 1949, **17**, 128.

[9] R. R. Randle and D. H. Whiffen, " Molecular Spectroscopy," Institute of Petroleum, London, 1955, p. 111.

group can be assigned by inspection of the published Tables.[9] In addition, the bands at 2154 and 523 cm.$^{-1}$ in the infrared can be associated with the C≡N and Se–C(N) stretching modes, respectively. The assignment of the six substituent-sensitive vibrations was made by comparison with the data for bromobenzene.[9] The infrared bands observed at 349 and 390 cm.$^{-1}$ were selected as the two Se–C≡N bending modes by comparison with methyl selenocyanate.

Phenylmercury(II) *Selenocyanate.*—If the phenylmercury(II) selenocyanate molecule is considered to have C_s symmetry, then the 39 fundamentals which are all active in both the infrared and Raman regions can be described in the following terms: 30 phenyl-group vibrations, three stretching vibrations, *viz.*, Hg–Se, Se–C, and C≡N, an in-plane and an out-of-plane Se–C≡N bend, an in-plane and an out-of-plane C–Hg–Se bend, an in-plane Hg–Se–C bend and a torsional mode. The observed bands, together with suggested assignments, are listed in Table 4.

TABLE 4

The infrared spectrum of phenylmercury(II) selenocyanate *

ν (cm.$^{-1}$)	Assignment
3070sh,w	C–H stretches
3061sh,w	
3048w	
3040w	
2129s	^{12}C≡N stretch
2083sh,vw	^{13}C≡N stretch (calculated 2084 cm.$^{-1}$)
1954vw	Phenyl combination bands
1879vw	
1867vw	
1621w	C–C stretch k
1575w	C–C stretch l split by crystal field
1571sh,w	
1479m	C–C stretch m split into doublet by crystal field
1477sh,m	
1432s	C–C stretch n
1399w	1026 + 373 = 1399?
1384w	2 × 694 = 1388
1329w	C–C stretch o
1303vw	246 + 1064 = 1310?
1193vw	In-plane C–H deform. a
1162w	In-plane C–H deform. c
1083w	694 + 389 = 1083? and in-plane C–H deform. d
1064	694 + 373 = 1067?
1026m	In-plane C–H deform. b and substituent-sensitive vibration q
1018m	
999m	In-plane ring deform. p
727s	Out-of-plane CH deform. f
694s	Out-of-plane ring deform. v
662w	Substituent sensitive vibration r?
616w	In-plane ring deform. s
542w	Se–C stretch
461sh,w	Substituent-sensitive vibration y
455m	
389m	In-plane Se–C≡N bend
373s	Out-of-plane Se–C≡N bend
246s	Hg–Se stretch and substituent-sensitive vibration t

* The compound was examined as a mull with Nujol or hexachlorobutadiene except in the 700—740 cm.$^{-1}$ region, when a solution in methylene chloride was used in order to remove the crystal-field splitting of the 727 cm.$^{-1}$ band.

The infrared spectrum of phenylmercury(II) iodide in the region 200—400 cm.$^{-1}$ shows a single strong band at 242 cm.$^{-1}$ which can reasonably be assigned to the substituent-sensitive phenyl vibration, t.[9] However, the Hg–Se stretching vibration in mercury(II) selenocyanate is observed at 228 and 231 cm.$^{-1}$, and hence the band at 246 cm.$^{-1}$ in the spectrum of phenylmercury(II) selenocyanate is assigned to one or both of these fundamentals.

EXPERIMENTAL

Solvents were dried by conventional methods. Other compounds were made and purified as follows:

Diphenylmercury. This was prepared [10] from sodium amalgam and bromobenzene and the

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[10] H. O. Calvery, *Org. Synth.*, 1929, **9**, 54.

product purified by repeated vacuum sublimation; it had m. p. 125° (lit.,[11] 125°) [Found: Hg, 56·5. Calc. for $(C_6H_5)_2Hg$: 56·5%].

Dimethylmercury. This was prepared from methylmagnesium iodide and mercury(II) chloride [12] [Found: Hg, 86·4. Calc. for $(CH_3)_2Hg$: Hg, 87·0%].

Mercury(II) *selenocyanate.* This was prepared by the addition of the appropriate quantity of aqueous potassium selenocyanate to an aqueous solution of mercury(II) nitrate buffered with ammonium acetate. The dried precipitate was a cream-coloured powder [Found: Se, 38·8. Calc. for $Hg(SeCN)_2$: Se, 38·5%]. The infrared spectrum of mercury(II) selenocyanate in Nujol showed bands at 2140s and 2130s (C≡N stretches), 541m (Se–C asym. stretch), 385m and 361s (Se–C≡N bends), 231vs and 228sh, s cm.$^{-1}$ (Hg–Se asym. stretch).

Phenylmercury(II) *cyanide.* This was prepared by refluxing equimolar quantities of mercury(II) cyanide and diphenylmercury in benzene for 18 hr. The product was recrystallised from alcohol to give a white crystalline solid, m. p. 209·5° (lit.,[13] 209°). The infrared spectrum of phenylmercury(II) cyanide was obtained by the KBr-disc technique in the range 4000—400 cm.$^{-1}$, and by use of a Nujol mull in the range 400—200 cm.$^{-1}$. The following bands were observed: 3068m, 3044w, 3031w, 2992m, 2165vw, 1955w, 1895w, 1880w, 1820w, 1765w, 1643w, 1589w, 1480s, 1431s, 1401w, 1383m, 1333m, 1304w, 1197w, 1158w, 1084m, 1062m, 1027ms, 998ms, 909m, 864w, 732vs, 695s, 615w, 451s, 408sh, m, 388s, 308m, and 244m cm.$^{-1}$.

These are essentially the bands expected for a monosubstituted benzene and their assignments follow closely those for phenylmercury(II) selenocyanate in Table 4. The C≡N stretch was observed at 2177 cm.$^{-1}$ in the spectrum of a solution of the compound in methylene chloride.

Phenylmercury(II) *iodide.* This was prepared by heating equimolar quantities of diphenylmercury and mercury(II) iodide under reflux in chloroform for 4 hr. The product was crystallised from toluene to give white crystals of phenylmercury(II) iodide, m. p. 263° (lit.,[14] 266°). The infrared spectrum of the compound was obtained (KBr disc) in the range 4000—400 cm.$^{-1}$ band and as a Nujol mull in the 400—200 cm.$^{-1}$ region. The observed bands, which are listed below, can be readily assigned by comparison with those of phenylmercury(II) selenocyanate and the published Tables: [9] 3048m, 3027m, 2986vw, 1868w, 1564m, 1469ms, 1423s, 1376w, 1320w, 1291w, 1154w, 1056w, 1008s, 990s, 901w, 718vs, 714vs, 686s, 650w, 606vw, 444s, and 242s cm.$^{-1}$.

Selenium selenocyanate and selenium dicyanide. These were prepared by disproportionation of selenocyanogen, produced in benzene solution by the action of iodine on an excess (5%) of silver selenocyanate.[15] The selenium dicyanide was sublimed under high vacuum from the mixture of selenium selenocyanate and selenium dicyanide and the non-volatile residue was recrystallised from benzene in an atmosphere of dry nitrogen to yield small golden-yellow crystals of selenium selenocyanate [Found: Se, 82·8. Calc. for $Se(SeCN)_2$: Se, 82·0%]. Selenium dicyanide was resublimed under high vacuum to give colourless crystals of pure material [Found: Se, 60·0. Calc. for $Se(CN)_2$: Se, 60·3%].

Methyl selenocyanate. This was prepared from methyl iodide and potassium selenocyanate.[16] The product was purified by triple precipitation from a cold solution in petroleum by cooling it to −78°, and finally by distillation under reduced pressure at room temperature from anhydrous magnesium sulphate. The compound was a foul-smelling, very pale straw-coloured liquid, m. p. −7° (Found: Se, 65·3. Calc. for CH_3SeCN: Se, 65·8%).

Phenyl selenocyanate. This was prepared from phenyldiazonium chloride and potassium selenocyanate in a sodium acetate buffer.[17] The product was decolourised by precipitation from petroleum at low temperature as described above, and after short-path vacuum-distillation from anhydrous magnesium sulphate the compound was obtained as a pale straw-coloured oil, m. p. −0·5° (Found: Se, 43·9. Calc. for C_6H_5SeCN: Se, 43·4%).

Reaction between Diphenylmercury and Selenium Selenocyanate.—A solution of diphenylmercury (6·04 g., 17·02 mmole) in benzene was added to a hot (80°) solution of selenium selenocyanate (4·92 g., 17·02 mmole) in benzene. The mixture was heated under reflux for 10 min. and then the black precipitate, which contained 90·8% Se (1·52 g., 17·50 mmole), was filtered off.

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[11] G. E. Coates, " Organo-Metallic Compounds," Methuen and Co. Ltd., London, 1960, p. 80.
[12] H. Gilman and R. E. Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 3314.
[13] E. Carr, I. B. Johns, and R. M. Hixon, *J. Amer. Chem. Soc.*, 1938, **60**, 891.
[14] " Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., 1961—1962.
[15] H. P. Kaufmann and F. Kögler, *Ber.*, 1926, **59**, 178.
[16] H. Stolte, *Ber.*, 1886, **19**, 1577.
[17] O. Behaghel and H. Seibert, *Ber.*, 1932, **65**, 815.

The yellow filtrate was evaporated under reduced pressure to yield a greasy, off-white solid, which was extracted with light petroleum. The petroleum extract was evaporated under reduced pressure to give a yellow oil which was purified by short-path vacuum-distillation at room temperature. The infrared spectrum of the pale straw-coloured oil (2·79 g., 15·3 mmole, 90% yield) indicated that it was phenyl selenocyanate (Found: Se, 43·1. Calc. for C_6H_5SeCN: Se, 43·1%). The buff-coloured, petroleum-insoluble material was dissolved in hot benzene and the filtered solution allowed to cool in the dark. Light petroleum was added to precipitate more *phenylmercury*(II) *selenocyanate* as a white powder. The compound (5·54 g., 14·5 mmole, 85% yield) had an infrared spectrum identical with that of the product from the metathesis reaction described below (Found: C, 23·2; H, 1·5; N, 5·3; Hg, 52·9; Se, 20·3. $C_6H_5HgSeCN$ requires: C, 22·0; H, 1·3; N, 3·7; Hg, 52·4; Se, 20·6%).

The molecular weight of phenylmercury(II) selenocyanate in *ca.* 0·02M-solution in benzene was found to be 410 (calc. *M*, 383) by using a Mechrolab Vapour Pressure Osmometer model 301A.

Preparation of Phenylmercury(II) *Selenocyanate by Metathesis.*—A suspension of mercury(II) selenocyanate (3·06 g., 7·46 mmole) and diphenylmercury (2·65 g., 7·46 mmole) in benzene was heated to the boiling point and kept for 30 min. in the dark. The liquid was then reheated to the boiling point and filtered. Phenylmercury(II) selenocyanate (4·75 g., 12·4 mmole, 83% yield) was obtained from the filtrate, by the method described above, as a white powder (Found: Se, 21·0. Calc. for $C_6H_5HgSeCN$: Se, 20·6%).

Reaction between Diphenylmercury and Selenium Dicyanide.—Selenium dicyanide (1·18 g., 9·05 mmole) and diphenylmercury (3·21 g., 9·05 mmole) were dissolved in benzene and the colourless solution was heated under reflux for 10 min. and then set aside for 4 weeks. The mixture was then heated under reflux for 1 hr. and the benzene removed from the cooled liquid by evaporation under reduced pressure. The off-white residue was extracted with light petroleum, and the solvent then removed from the extract by evaporation under reduced pressure. About 1 ml. of yellow oil remained, and this was distilled under vacuum at room temperature to give a pale straw-coloured oil (1·29 g., 7·08 mmole, 78% yield), identified on the basis of its infrared spectrum as pure phenyl selenocyanate.

The petroleum-insoluble reaction product was identified from its infrared spectrum as phenylmercury(II) cyanide, containing no detectable quantities of phenylmercury(II) selenocyanate. The compound was recrystallised from ethanol to give small white crystals (2·46 g., 8·08 mmole, 89% yield), which did not depress the melting point of an authentic sample of phenylmercury(II) cyanide.

Reaction between Dimethylmercury and Selenium Selenocyanate.—A solution of dimethylmercury (2·50 g., 10·8 mmole) in cold benzene was added to a hot (80°) solution of selenium selenocyanate (3·13 g., 10·8 mmole) in benzene and the mixture was heated under reflux for 6 hr. During this time a black precipitate containing 95% selenium (1·11 g., 13·4 mmole Se) was deposited slowly. After the precipitate had been filtered off the pale yellow filtrate was evaporated to 30 ml. under reduced pressure. This solution was then crudely fractionated under vacuum, and a colourless oil was obtained which was identified from its infrared spectrum as methyl selenocyanate (0·36 g., 2·99 mmole, 28% yield).

The involatile, oily, brown residue was dissolved in cold benzene and filtered into well-stirred light petroleum, *methylmercury*(II) *selenocyanate* being precipitated as a white crystalline powder. The precipitate had an infrared spectrum identical to that of the product of the metathetical reaction between dimethylmercury and mercury(II) selenocyanate (Found: C, 7·5; H, 1·0; N, 4·5; Hg, 62·6; Se, 24·2. $CH_3HgSeCN$ requires: C, 7·5; H, 0·9; N, 4·4; Hg, 62·6; Se, 24·6%). The molecular weight of the air-sensitive compound was determined cryoscopically in benzene (Found: *M*, 336. Calc.: *M*, 320·6).

Preparation of Methylmercury(II) *Selenocyanate by Metathesis.*—Dimethylmercury (2·04 g., 8·86 mmole), and mercury(II) selenocyanate (3·64 g., 8·86 mmole) were shaken in cold benzene and the suspension heated to the boiling point and allowed to cool in the dark. The liquid was then filtered slowly into well-stirred light petroleum, methylmercury(II) selenocyanate (3·50 g., 10·91 mmole, 61% yield) being precipitated as a white crystalline powder (Found: Se, 24·8. Calc. for $CH_3HgSeCN$: Se, 24·6%).

Analysis.—Selenium was determined volumetrically by titration with standard potassium permanganate,[18] and nitrogen by the Kjeldahl method. Mercury in the presence of selenium was analysed by decomposition of a weighed sample with conc. nitric acid in a Carius tube at

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[18] F. A. Gooch and C. F. Clemons, *Amer. J. Sci.*, 1895, **50**, 51.

250°. Mercury in the diluted nitric acid solution was determined by titration in a hexamine buffer with standard e.d.t.a. and Xylenol Orange as indicator.

Infrared and Raman Measurements.—Infrared spectra were obtained with a Perkin-Elmer 125 grating infrared spectrophotometer in the range 4000—400 cm.$^{-1}$, and a Grubb–Parsons DM4 spectrophotometer in the region 450—200 cm.$^{-1}$. Raman spectra were obtained on a Hilger model 612 Raman spectrometer, incorporating two glass prisms and a specially designed Toronto arc source; the output was connected to a Honeywell–Brown recorder. The exciting line was the 4358 Å mercury line, and a saturated solution of aqueous potassium nitrite was used as a filter. The observed frequencies were calibrated from the position of appropriate strong bands in the spectra of carbon tetrachloride, chloroform, and benzene and are correct within ±2 cm.$^{-1}$ for all but the weak and broad bands. Polarisation measurements were obtained by the method of polarised incident light.

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