

Selenium Derivatives in the Indole Series

IV.* Mass Spectrometric Investigation of 3-Selenocyanatoindole, 3,3'-Diindolyl Diselenide, and their 1-Methyl- and 2-Methyl-Derivatives

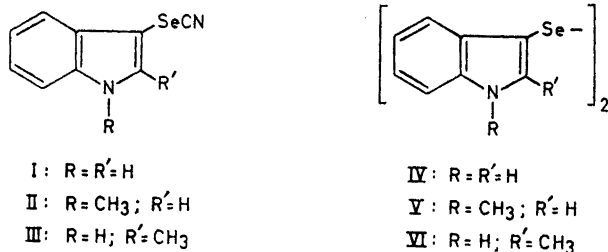
LARS-BÖRGE AGENÄS

Chemical Institute, University of Uppsala, Uppsala, Sweden

The mass spectra of 3-selenocyanatoindole (I), 1-methyl-3-selenocyanatoindole (II), 2-methyl-3-selenocyanatoindole (III), and the corresponding diselenides, 3,3'-diindolyl diselenide (IV), 3,3'-di-(1-methyl-indolyl) diselenide (V), and 3,3'-di-(2-methyl-indolyl) diselenide (VI), have been recorded and these spectra are reported and discussed. The selenocyanato compounds show a fragmentation analogous to other aromatic selenocyanates, thus splitting off the selenocyanato substituent in two steps, the remaining ion further fragmenting as has been earlier described for indole and alkyl substituted indoles. The diselenides are fragmented like other aromatic diselenides and split off the two selenium atoms in two steps. The remaining ion, biindolyl, is further fragmented in the expected way. All the spectra show signs of other fragmentation paths, which are discussed in the paper.

After the construction of mass spectrometers suitable for the investigation of organic compounds, the development of the mass spectrometry within this field has been very rapid. Much information on most types of organic compounds and their mass spectrometry is available today. Among other groups, organo-sulphur compounds have lately been extensively investigated. The analogous organo-selenium compounds have not so far been investigated with mass spectrometry. The mass spectra of a few organo-selenium compounds have been published¹⁻³ in investigations of different heterocyclics. Recently, an investigation of organo-selenium compounds by mass spectrometry was started in this Institute. The first part of this work is published in a preceding paper,⁴ and deals with the fragmentation of some seleno substituted, simple aromatic compounds. Simultaneously, the present investigation has been performed. This paper deals with the mass spectra of some seleno substituted indoles, *i.e.* 3-selenocyanatoindole (I), 1-methyl-3-selenocyanatoindole (II), 2-methyl-3-selenocyanatoindole (III), and the cor-

* Part III. *Arkiv kemi* 23 (1964) 155.



Scheme 1.

responding diselenides 3,3'-diindolyl diselenide (IV), 3,3'-di-(1-methyl-indolyl) diselenide (V), and 3,3'-di-(2-methyl-indolyl) diselenide (VI).

SELENOCYANATO-INDOLES

The mass spectra of the three selenocyanato substituted indoles investigated (I-III) are given in Figs. 1-3. The spectra are very similar leading to the conclusion that the compounds are fragmented similarly. In all the spectra, characteristic groups of peaks are found to be centered around mass numbers corresponding to the molecular ion (M), M-26, M-80, and M-106. These four groups of peaks, which have been found in the mass spectra of other types of aromatic selenocyanates,^{4,5} are very specific for selenocyanato substituted compounds in the aromatic series. The groups of peaks occurring from the formation of selenium containing fragment ions show internal intensities well in agreement with the natural abundances of the stable selenium isotopes.* In the following discussion, the peak corresponding to the main

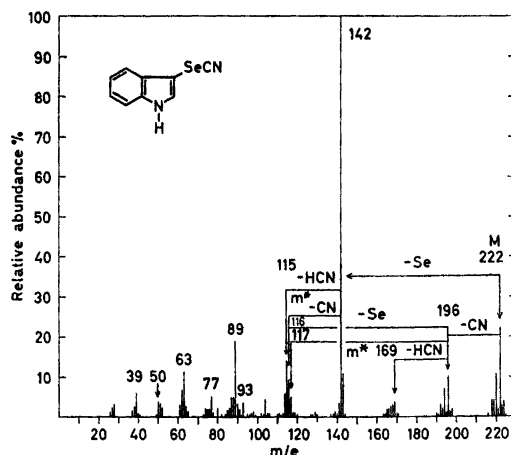


Fig. 1. Mass spectrum of 3-selenocyanatoindole (I), recorded with the ion source at 55°.

* ⁷⁴Se: 0.87, ⁷⁶Se: 9.02, ⁷⁷Se: 7.58, ⁷⁸Se: 23.52, ⁸⁰Se: 49.82, ⁸²Se: 9.19.⁶

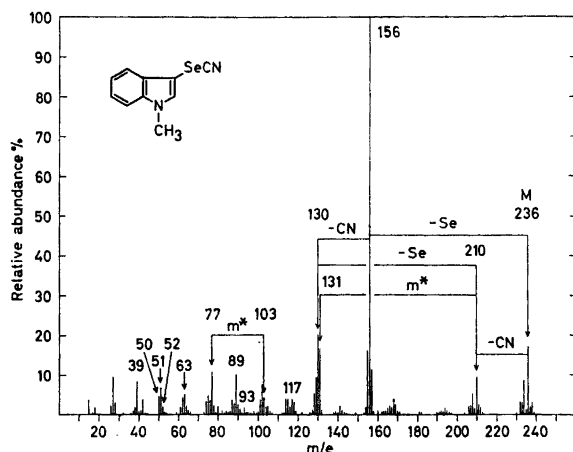


Fig. 2. Mass spectrum of 1-methyl-3-selenocyanatoindole (II), recorded with the ion source at 40°.

selenium isotope ^{80}Se will be considered as representing the selenium containing fragment in question. The groups of peaks in Figs. 1–3 correspond to the fragmentation of the molecular ion by the loss of a cyanide fragment (M–26), the loss of a selenium atom (M–80), and the loss of the selenocyanato group (M–106), the formation of these fragments suggests the fragmentation paths given in Scheme 2 for 3-selenocyanatoindole (I). Two alternative routes for the formation of the M–106 fragment ions are possible as found from the mass spectra recorded. The methyl substituted analogues II and III are being fragmented in the same way and the fragment ions corresponding

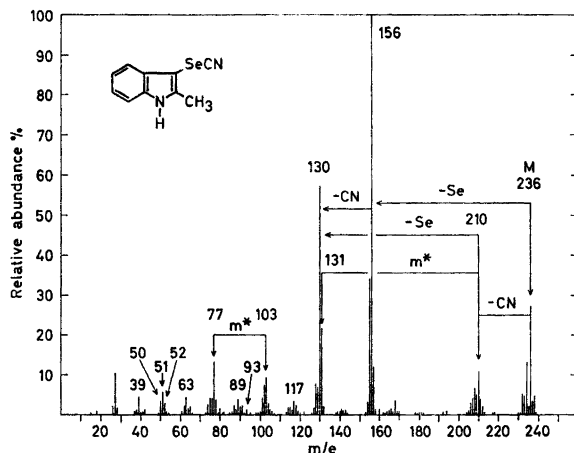
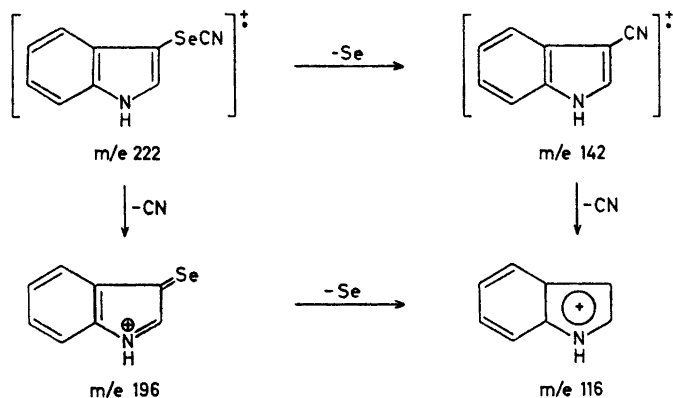


Fig. 3. Mass spectrum of 2-methyl-3-selenocyanatoindole (III), recorded with the ion source at 50°.



Scheme 2.

to those in Scheme 2 occur at 14 mass units higher. The base peaks of the spectra in Figs. 1—3 are in all the three cases the $M-80$ fragment peak.

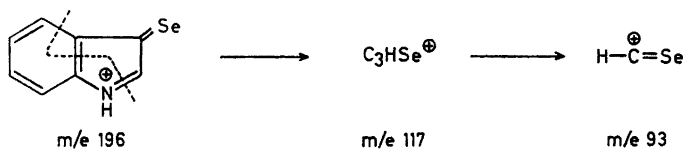
When the spectrum of I is studied in detail, it is found that besides the peak at m/e 116 caused by the formation of the indolylic ion in Scheme 2, other fragments give peaks at the adjacent mass numbers. The most abundant ion within this group is m/e 115, which is explained by the loss of a hydrogen atom from the indolylic ion at m/e 116. More interesting is the occurrence of the fragment at m/e 117. The presence of a selenium containing fragment must have its origin in a fragmentation very similar to what was found to occur in the case of phenyl selenocyanate.⁴ The proposed explanation is given in Scheme 3.

These proposed fragmentations are further supported by the presence of metastable peaks at m/e 69.2 and 93.2. The lower value is in good agreement with the calculated value 69.8 for the first fragmentation step in Scheme 2, and the other metastable peak similarly agrees with the calculated value 93.1 for the loss of a hydrogen cyanide fragment from the ion at m/e 142.

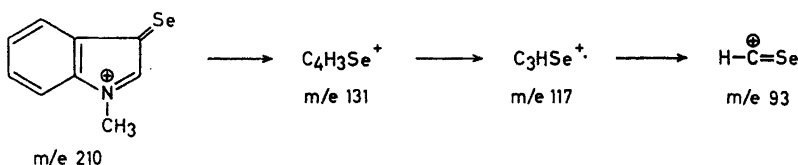
Finally, the fragment at m/e 169 in Fig. 1 must have been formed by another minor fragmentation path. The most reasonable explanation is the loss of a hydrogen cyanide fragment from the ion at m/e 196. This means breaking of the indole ring system. Similar fragmentations have been reported for indole and alkyl substituted indoles.

The resulting indolylic ion at m/e 116 is further fragmented in good agreement with the results from the investigation of indole and alkyl substituted indoles^{7,8} and the details from that part of the spectrum need no discussion in this paper.

A detailed study of the spectrum of II in Fig. 2 gives evidence of fragmentations similar to what was found for I when that spectrum was considered in detail. The peak caused by the indolylic ion at m/e 130 is found together with almost equivalent peaks at m/e 129 and 131. The peak with lower mass can be explained analogously to what was declared in the discussion of the spectrum of I and its origin is thus supposed to be the loss of a hydrogen



Scheme 3.



Scheme 4.

atom from the indolylic ion at m/e 130. Quite similarly, a peak at m/e 155 is observed and found to be caused by the loss of a hydrogen atom from the fragment at m/e 156.

The peak at m/e 131 is to be explained by a fragmentation path analogous to what was given for I in Scheme 3. In this case, the similar fragmentation must be connected with a rearrangement. The proposed explanation is given in Scheme 4. The suggested fragmentation is further supported by the presence of a selenium containing fragment at m/e 93 and a metastable peak at m/e 81.5. The metastable peak is in good agreement with the calculated value m/e 81.7 for the formation of the fragment at m/e 131 from the ion at m/e 210.

The detailed study of the spectrum of III in Fig. 3 gives a result analogous to what was found for II. Additional peaks are found at the same mass numbers and the same explanation thus follows. The same fragmentation as was given in Scheme 4 is the origin to the peaks at m/e 131 and 93, but the rearrangement step must be excluded as the appropriate structure for the formation of the fragment at m/e 131 already is found in the ion at m/e 210 in the case of III. The fragmentation is also here supported by the metastable peak observed at m/e 81.5 of the spectrum in Fig. 3.

Additional metastable peaks are found in the spectra of II and III at m/e 57.5. This peak in each spectrum is ascribed to the fragmentation of the indolylic ion, as the value is in good agreement with the calculated value 57.6 for the formation of the ion at m/e 77 from the fragment at m/e 103.

DIINDOLYL DISELENIDES

The mass spectra of the three diselenides IV, V, and VI, corresponding to the selenocyanates already discussed, have been recorded and are given in Figs. 4–6. These three spectra are also very similar in nature and the fragmentation of the diselenides is supposed to proceed along the same path. The spectra are composed of a series of characteristic peaks, which was found

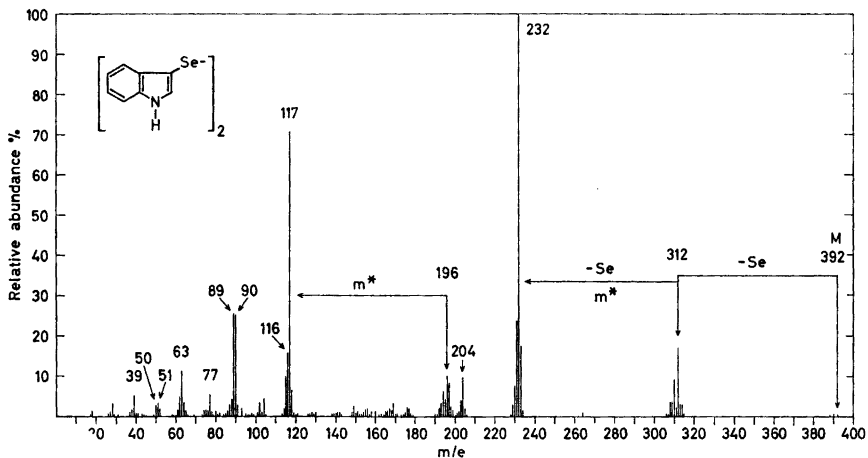


Fig. 4. Mass spectrum of 3,3'-diindolyl diselenide (IV), recorded with the ion source at 90°.

also in the investigation of the mass spectra of other types of aromatic diselenides.^{4,5} Independent of this investigation, Bergman⁹ has studied the mass spectra of the monoselenides corresponding to IV and V. His spectra are in good agreement with those obtained in the present investigation, and his results are published simultaneously with this paper. Aromatic disulphides have been studied by Bowie *et al.*;¹⁰ the fragmentations of the disulphides are similar to what has been found for diselenides.⁴

The characteristic peaks of the spectra in Figs. 4-6 are occurring at mass numbers corresponding to molecular weight (M), M-80, M-160, M/2, and

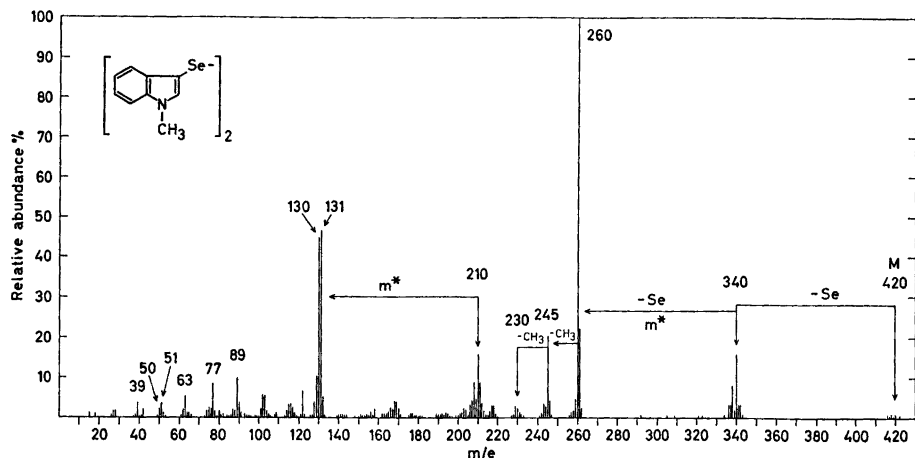


Fig. 5. Mass spectrum of 3,3'-di-(1-methyl-indolyl) diselenide (V), recorded with the ion source at 55°.

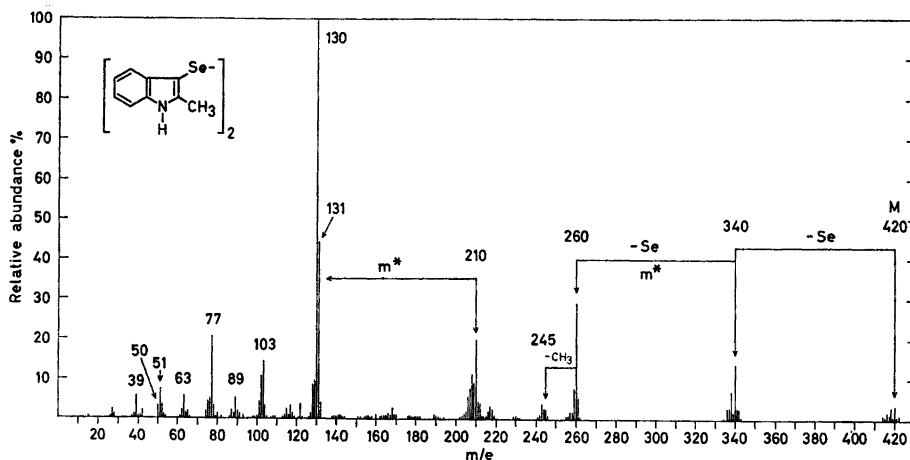
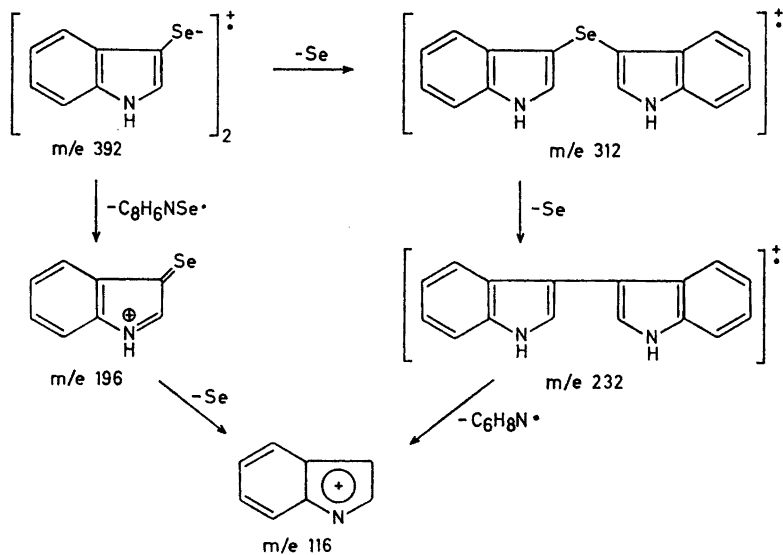


Fig. 6. Mass spectrum of 3,3'-di-(2-methyl-indolyl) diselenide (VI), recorded with the ion source at 140°.

(M/2)-80. The analogous fragments have been found in the spectra of diphenyl diselenide and 4,4'-dimethyl-diphenyl diselenide.⁴ The observation of this series of peaks suggests the fragmentation paths given in Scheme 5 for the case of IV.



Scheme 5.

The formation of the simple indolylic ion thus proceeds along two different paths. The molecular ion is fragmented by the loss of a selenium atom, forming

a monoselenide fragment, at m/e 312 ($M-80$), and this is further fragmented to give a biindolyl ion by the loss of the second selenium atom ($M-160$). The biindolyl is finally split into halves to give the indolylic ion at m/e 116 [$(M/2)-80$]. The alternative path is the splitting of the molecular ion into identical halves ($M/2$), which then give the fragment at m/e 116 by the loss of selenium. The corresponding peaks in the spectra of V and VI occur at mass numbers 14 units higher. The formation of the monoselenide ion at m/e 312 as an intermediate to the biindolyl ion at m/e 232 is further supported by the metastable peak observed at m/e 172.5, whose value is equal to what has been calculated for the formation of the biindolyl ion at m/e 232 from the monoselenide ion at m/e 312. The spectra of V and VI similarly show metastable peaks at m/e 199.5, in good agreement with the calculated value 198.8 for the formation of the corresponding biindolyl from the intermediate monoselenides. The base peaks of the spectra of IV and V are the $M-160$ ions, *i.e.* the biindolyl ions, while in the spectrum of VI the base peak occurs as the $(M/2)-80$ fragment peak, *i.e.* the final indolylic ion. A possible explanation to this dissimilarity is steric hindrance of the two methyl groups in the 2- and 2'-positions making the biindolyl in the case of VI considerably less stable than in the cases of IV and V.

Considering the three spectra in Figs. 4–6 in detail, the same minor peaks as were found in the spectra of the corresponding selenocyanates are observed, leading to the fragmentations given in Schemes 3 and 4. However weak, the occurrence of the peaks also in the spectra of the diselenides gives further support to the proposed fragmentation routes. As in the spectra of the selenocyanates, the spectra in Figs. 4–6 show metastable peaks at m/e 69.4 and 81.5, respectively, further supporting the fragmentations suggested.

The three diselenide spectra are further found to have peaks at $M-161$, leading to the suggestion that the second selenium atom can be lost by an alternative path as a HSe-fragment. Finally, a weak group of peaks at m/e 80 is found in all the three spectra, corresponding to a selenium fragment.

In the spectrum of IV in Fig. 4 a comparatively intense peak is found at m/e 204. The most reasonable origin of this peak is the loss of a H_2CN fragment, possibly in two succeeding fragmentation steps. The two methyl substituted diselenides can also split-off the methyl groups which is evident from the weak peaks as indicated in Figs. 5–6.

The indole residues are fragmented as has been earlier described for simple indole molecules,^{7,8} and these parts of the spectra need no further discussion.

EXPERIMENTAL

The mass spectra were recorded using an LKB model 9000A gas chromatograph-mass spectrometer. All the spectra were recorded using the direct inlet technique. The temperatures used for the vaporization of the samples have been indicated in connection with the figures. The electron energy was 70 eV.

The purity of the materials investigated was determined by microanalysis for selenium, using a method developed by Bengtsson,¹⁰ which is very similar to the method of Gould.¹¹

3-Selenocyanatoindole (I) was prepared by the direct selenocyanation method as described earlier.¹² M.p. 98.5–100°

1-Methyl-3-selenocyanatoindole (II) was prepared analogously to I as earlier described.¹³ M.p. 108–109°.

2-Methyl-3-selenocyanatoindole (III) was prepared analogously to I as earlier described.¹³ M.p. 126–127°.

3,3'-Diindolyl diselenide (IV) was prepared by treating I with alkali as earlier described.¹² M.p. 178–179.5°.

3,3'-Di-(1-methyl-indolyl) diselenide (V) was prepared analogously to IV as earlier described.¹³ M.p. 118–120°.

3,3'-Di-(2-methyl-indolyl) diselenide (VI) was prepared analogously to IV as earlier described.¹³ M.p. 183–184°.

Acknowledgements. I wish to express my sincere gratitude to Professor Arne Fredga for his constant interest in this project. I am also very grateful for the facilities he has placed at my disposal. I am indebted to Dr. K. Ohlsson for very valuable discussions and to Dr. S.-O. Lawesson for his kind interest and advice. My thanks are also due to Professor Folke Nydahl for the facilities he has placed at my disposal, making the microanalyses for selenium possible. A grant from *AB Astra, Södertälje, Sweden* is gratefully acknowledged. The selenium analyses were performed by Mrs. Marie Ljungquist.

REFERENCES

1. Duffield, A. M., Budzikiewicz, H. and Djerassi, C. *J. Am. Chem. Soc.* **87** (1965) 2920.
2. Buu-Hoi, N. P., Jacquignon, P. and Mangano, M. *Chem. Commun.* **1965** 624.
3. Svec, H. J. and Junk, G. A. *J. Am. Chem. Soc.* **89** (1967) 790.
4. Agenäs, L.-B. *Acta Chem. Scand.* **22** (1968) 1763.
5. Agenäs, L.-B. *To be published.*
6. Beynon, J. H. *Mass Spectrometry and its Application to Organic Chemistry*, Elsevier, Amsterdam 1960, p. 558.
7. Beynon, J. H. and Williams, A. E. *Appl. Spectry.* **13** (1959) 101.
8. Beynon, J. H. and Williams, A. E. *Appl. Spectry.* **14** (1960) 27.
9. Bergman, J. *Acta Chem. Scand.* **22** (1968) 1883.
10. Bowie, J. H., Lawesson, S.-O., Madsen, J. Ø., Nolde, C., Schroll, G. and Williams, D. H. *J. Chem. Soc. Sect. B* **1966** 946.
11. Bengtsson, A. *To be published.*
12. Gould, E. S. *Anal. Chem.* **23** (1951) 1502.
13. Agenäs, L.-B. *Acta Chem. Scand.* **17** (1963) 268.
14. Agenäs, L.-B. *Arkiv Kemi* **23** (1964) 155.

Received January 24, 1968