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CYANOHYDRINS IN CARBON-TRAPPED VAPOR PHASE OF CIGARETTE SMOKE

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ABSTRACT

The cyanohydrins of acetaldehyde, propionaldehyde and isobutyraldehyde have been isolated as the trimethylsilyl ethers from carbon-trapped vapor phase of cigarette smoke. Relative molar ratios of these ethers were, respectively, about 5:2:1. Identifications were accomplished by spectral and GLC comparisons of the isolated materials with synthetic samples. The trimethylsilyl ether of acrolein cyanohydrin was absent in the smoke-derived ethers samples.

INTRODUCTION

Nall and Roscoe(1) recently presented compelling evidence for the occurrence of complexed hydrogen cyanide in carbon traps containing the vapor phase of cigarette smoke. They concluded from the observed chemistry that aldehyde cyanohydrins were the major complexes and postulated that these cyanohydrins may also be responsible for the high retention of hydrogen cyanide on Cambridge filters. Lactonitrile (acetaldehyde cyanohydrin) was presumed to be the major complex since acetaldehyde is the major vapor phase aldehyde in smoke. In this report we wish to describe the isolation and identification of three cyanohydrins from carbon-trapped vapor phase of cigarette smoke.

EXPERIMENTAL

Preparation of Cyanohydrins - The cyanohydrins of propionaldehyde, isobutyraldehyde and acrolein were prepared by adding potassium cyanide to a mixture of the aldehyde and acetic acid in anhydrous ether. In a typical preparation, 3.3 g. of potassium cyanide was added in one batch to a mixture of 2.5 ml. of propionaldehyde and 3.0 ml. of acetic acid in 20 ml. of anhydrous ether. A slightly exothermic reaction was noted and a white precipitate of potassium acetate was formed. The reaction mixture was filtered after 15 min., and the filtrate was concentrated on a rotary evaporator at $60^\circ/10$ mm. to give residual propionaldehyde cyanohydrin.

Portions of the cyanohydrins were trimethylsilylated and the resulting trimethylsilyl ethers were isolated by GLC on either Carbowax 20M or SE-30 columns.

Trimethylsilylation of Cyanohydrins(2) - A 50 µl. sample of lactonitrile was dissolved in 1.0 ml. of dry pyridine, and to this was added 200 µl. of hexamethyldisilazane and 100 µl. of trimethylchlorosilane. After shaking and letting the reaction mixture sit for 5 min., a 75 µl. aliquot was separated by GLC on a Carbowax 20M column at 150°. The trimethylsilyl ether of lactonitrile was eluted before pyridine and was collected.

The trimethylsilyl ethers of propionaldehyde, isobutyraldehyde and acrolein cyanohydrins were similarly prepared. These were isolated by GLC on a SE-30 column at 132°.

Trimethylsilyl Ethers from Vapor Phase Carbon Traps - Carbon from 40 vapor phase traps on smoking machines was obtained from the TPM group. This carbon had been used for over two weeks and subjected to the vapor phase from over 16,000 cigarettes. About 70% of this carbon was eluted with 300 ml. of methanol using a Büchner funnel and suction filtration. The filtrate (about 200 ml.) was concentrated to about 2.5 ml. on a rotary evaporator at 20°/10 mm., and this residue was trimethylsilylated with 25 ml. of pyridine, 7 ml. of hexamethyldisilazane and 3.5 ml. of trimethylchlorosilane. More hexamethyldisilazane and trimethylchlorosilane were added in portions until no more ammonium chloride was formed. The reaction mixture was then filtered and concentrated to 4.5 ml. by distillation through a Vigreaux column at 760 mm. GLC analysis showed that the trimethylsilyl ethers were in this concentrate.

The trimethylsilyl ethers were isolated from the concentrated product solution by GLC on a 12' x 3/8" 30% Carbowax 20M on 60/80 mesh Chromosorb W Column at 150°/20 psig He. Major peaks were eluted at 6.3 min. (Peak A, Ht. = 160), 7.6 min. (Peak B, Ht. = 85), 8.2 min. (pyridine, Ht. = 930), 9.8 min. (Ht. = 9) and 10.7 min. (Ht. = 17). Peaks A and B were collected.

Peak A gave a NMR spectrum identical with one from the authentic trimethylsilyl ether of lactonitrile, but the IR spectrum contained a few extra weak absorption bands. After repurification on a SE-30 column, the Peak A and lactonitrile trimethylsilyl ether IR spectra were identical. The isolated and synthetic samples had identical retention times on Carbowax 20M and SE-30 GLC columns.

Peak B was further resolved into two major components by GLC on a 6' x 1/4" 20% SE-30 on 60/80 mesh Chromosorb W column at 107°/15 psig He. Peak B-1 was eluted at 8.0 min. (Ht. = 32) and peak B-2 at 10.0 min. (Ht. = 40). IR and NMR spectra of the collected B-1 and B-2 samples were identical with those from the trimethylsilyl ethers of propionaldehyde and isobutyraldehyde cyanohydrins, respectively. Identical GLC retention times on SE-30 and XE-60 columns completed the identifications.

The concentrated pyridine solution of trimethylsilyl ethers did not show a peak corresponding in retention time with the trimethylsilyl ether of acrolein cyanohydrin on a SE-30 GLC column.

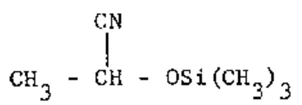
RESULTS AND DISCUSSION

The objective of this study was to confirm the presence of cyanohydrins in carbon-trapped vapor phase of smoke. Fortunately, the TPM group in these laboratories provided a source of carbon which had become saturated with the vapor phase of cigarette smoke, and no further smoking was required.

Nall and Rosene(1) had previously observed that lactonitrile decomposed on GLC, and other cyanohydrins would be expected to behave similarly. This thermal decomposition could be either by loss of water to form an unsaturated nitrile or by regeneration of hydrogen cyanide and the parent aldehyde. It appeared that the cyanohydrin trimethylsilyl ethers would have adequate thermal stability for GLC isolation and low enough polarity for use of high-resolution GLC columns. Moreover, the trimethylsilyl group provides an excellent internal standard for NMR studies.

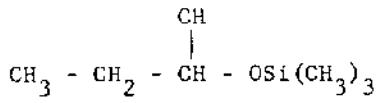
Cyanohydrins are readily hydrolyzed in hydroxylic solvents, particularly in basic solution. A preliminary experiment was devised to see what loss of lactonitrile occurred during concentration of a methanol solution. A solution containing 0.1 g. of lactonitrile in 200 ml. of methanol was concentrated to about 1 ml. on a rotary evaporator at 20°/10 mm., and an aliquot of this residue was trimethylsilylated. About 50% recovery was indicated by GLC analysis for lactonitrile trimethylsilyl ether. It appeared that this procedure should be equally applicable to smoke eluted from carbon columns.

The concentration procedure was applied to a methanol eluate from carbon which had been used to trap the vapor phase from about 10,000 cigarettes, and the resulting concentrate was trimethylsilylated. After concentration, the major trimethylsilyl ethers were isolated by GLC on Carbowax 20M and SE-30 columns. The major ether gave IR and NMR spectra and GLC retention times on two columns which were identical with those from a previously prepared sample of lactonitrile trimethylsilyl ether (I). The spectral characteristics of the other two products suggested them to be the trimethylsilyl ethers of propionaldehyde (II) and isobutyraldehyde (III) cyanohydrins, and these assignments were confirmed by synthesis. Final identifications were again based on identical IR and NMR spectra and GLC retention times on two columns. The GLC evidence indicated that the relative molar ratios of products were approximately I:II:III = 5:2:1.



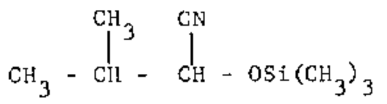
$CH_3 - \overset{CN}{\overset{|}{CH}} - OSi(CH_3)_3$

I



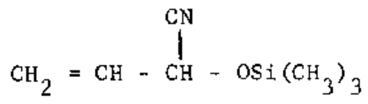
$CH_3 - CH_2 - \overset{CH}{\overset{|}{CH}} - OSi(CH_3)_3$

II



$CH_3 - \overset{CH_3}{\overset{|}{CH}} - \overset{CN}{\overset{|}{CH}} - OSi(CH_3)_3$

III



$CH_2 = CH - \overset{CN}{\overset{|}{CH}} - OSi(CH_3)_3$

IV

The trimethylsilyl ether of acrolein cyanohydrin (IV) was synthesized, but a corresponding GLC peak was absent in the SE-30 column chromatogram of the smoke derived ethers. This absence may possibly be due to the isolation procedure.

NMR spectra of I, II, III and IV in carbon tetrachloride solutions are presented, respectively, in Figures 1, 2, 3 and 4. The integrals and coupling patterns are, in each instance, consistent with the assigned structures. Major IR absorption bands for the four compounds are presented in Table 1. Cyanide absorption does not appear in any of the IR spectra due to the pronounced quenching effect of oxygen on the cyanide-bearing carbon(3).

GLC retention times for I, II, III, IV and pyridine on Carbowax 20M and SE-30 columns are presented in Table 2. In addition to the ethers I, II and III, the smoke-derived ethers solution showed several minor GLC peaks. It is to be expected that most of the aldehydes, and perhaps some of the ketones, would be involved in cyanohydrin formation on carbon.

The results of this study demonstrate that cyanohydrins are indeed present in carbon-trapped vapor phase of cigarette smoke. It is still not known if cyanohydrin formation is responsible for the high retention of hydrogen cyanide on particulate filters.

REFERENCES

1. J. F. Nall and C. J. Rosene, B&W Research Report #66-2.
2. C. C. Sweeley, R. Bentley, M. Makita and W. W. Wells, J. Am. Chem. Soc., 85, 2497 (1963).
3. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, 1958, page 266.

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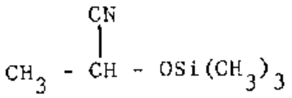
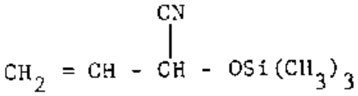
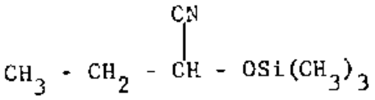
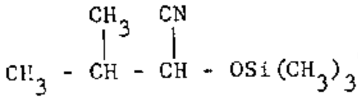
TABLE 1

MAJOR INFRARED ABSORPTION BANDS OF TRIMETHYLSILYL ETHERS[a]

Compound	Principal Absorption Bands[b]
 $CH_3-\overset{CN}{\overset{\vert}{CH}}-OSi(CH_3)_3$	848, 860, 1130, 967, 1252, 1065 $cm.^{-1}$
 $CH_2=CH-\overset{CN}{\overset{\vert}{CH}}-OSi(CH_3)_3$	845, 867, 1252, 1099, 939, 980, 1034 $cm.^{-1}$
 $CH_3-CH_2-\overset{CN}{\overset{\vert}{CH}}-OSi(CH_3)_3$	844, 874, 1252, 1132, 1112, 1016 $cm.^{-1}$
 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-\overset{CN}{\overset{\vert}{CH}}-OSi(CH_3)_3$[c]	848, 868, 1103, 1252, 1060 $cm.^{-1}$

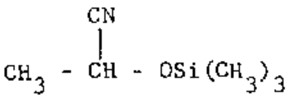
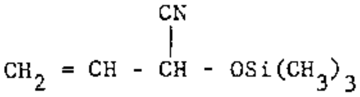
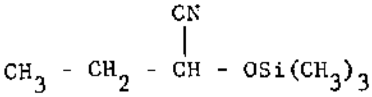
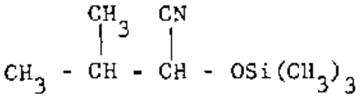
a) Spectra obtained in carbon tetrachloride solution with a Beckman Model IR-5 infrared spectrophotometer.

b) Principal discrete absorption maxima in order of decreasing intensity.

c) This compound also shows weak absorption at 1369 and 1388 $cm.^{-1}$ indicating the presence of gem-dimethyl functionality.

TABLE 2

GLC RETENTION CHARACTERISTICS OF TRIMETHYLSILYL ETHERS

Compound	SE-30[a]	Carbowax 20M[b]
Pyridine	7.2 min.	18.4 min.
 $CH_3-\overset{\overset{CN}{\vert}}{CH}-OSi(CH_3)_3$	10.3	13.8
 $CH_2=CH-\overset{\overset{CN}{\vert}}{CH}-OSi(CH_3)_3$	14.6	23.0
 $CH_3-CH_2-\overset{\overset{CN}{\vert}}{CH}-OSi(CH_3)_3$	15.3	17.1
 $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-\overset{\overset{CN}{\vert}}{CH}-OSi(CH_3)_3$	19.6	17.6

a) 12' x 3/8" 20% SE-30 on 60/80 mesh Chromosorb W column at 133°C. and helium flow rate of 120 cc./min.

b) 12' x 3/8" Carbowax 20M on 60/80 mesh Chromosorb W column at 130°C. and helium flow rate of 120 cc./min.

FIGURE 1

60 Mc. NMR SPECTRUM OF LACTONITRILE TRIMETHYLSILYL ETHER

m/e = 143.0767 $C_6H_{13}NOSi$ requires 143.0766
128.0554 $C_5H_{10}NOSi$ " 128.0532

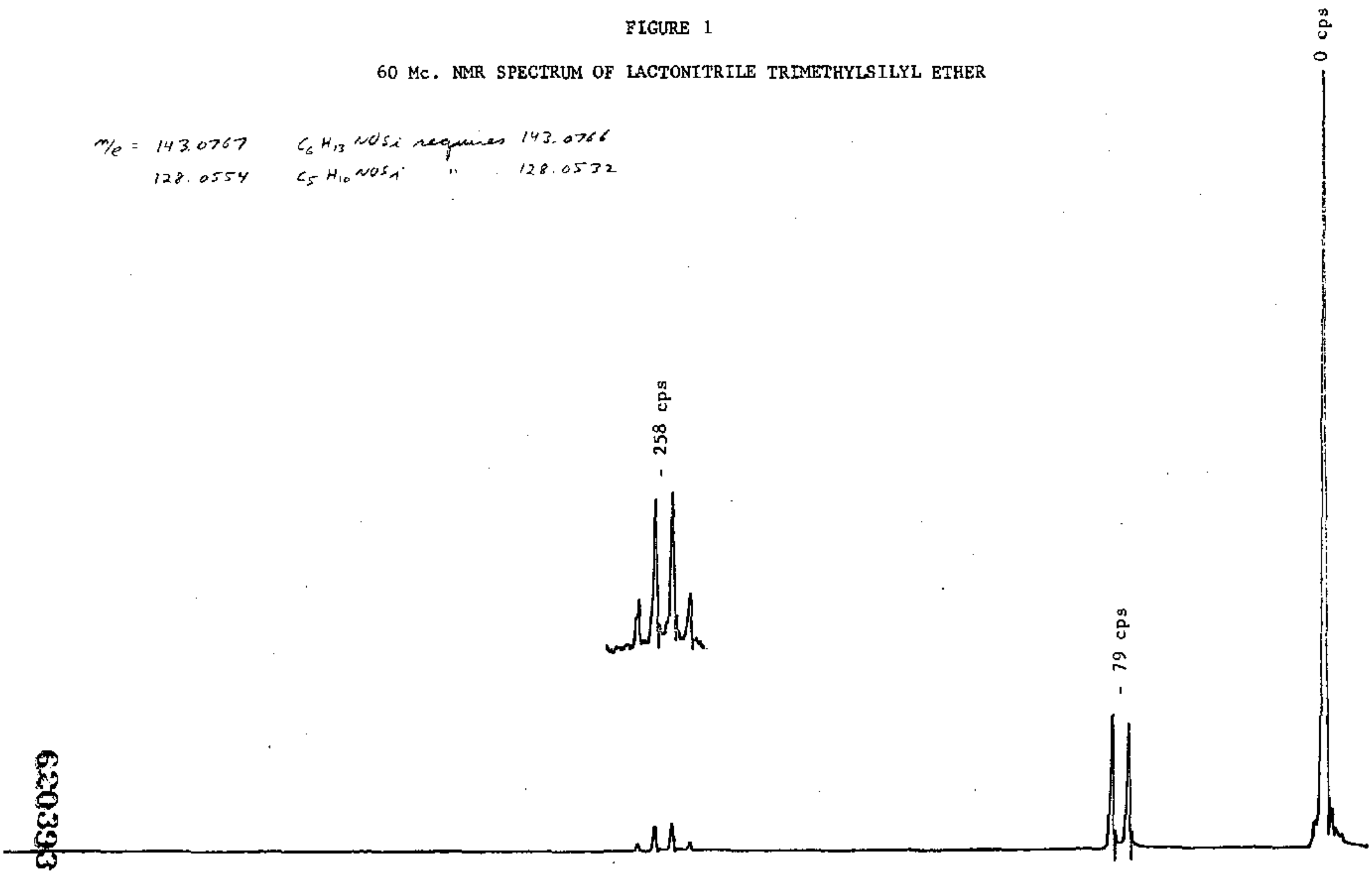
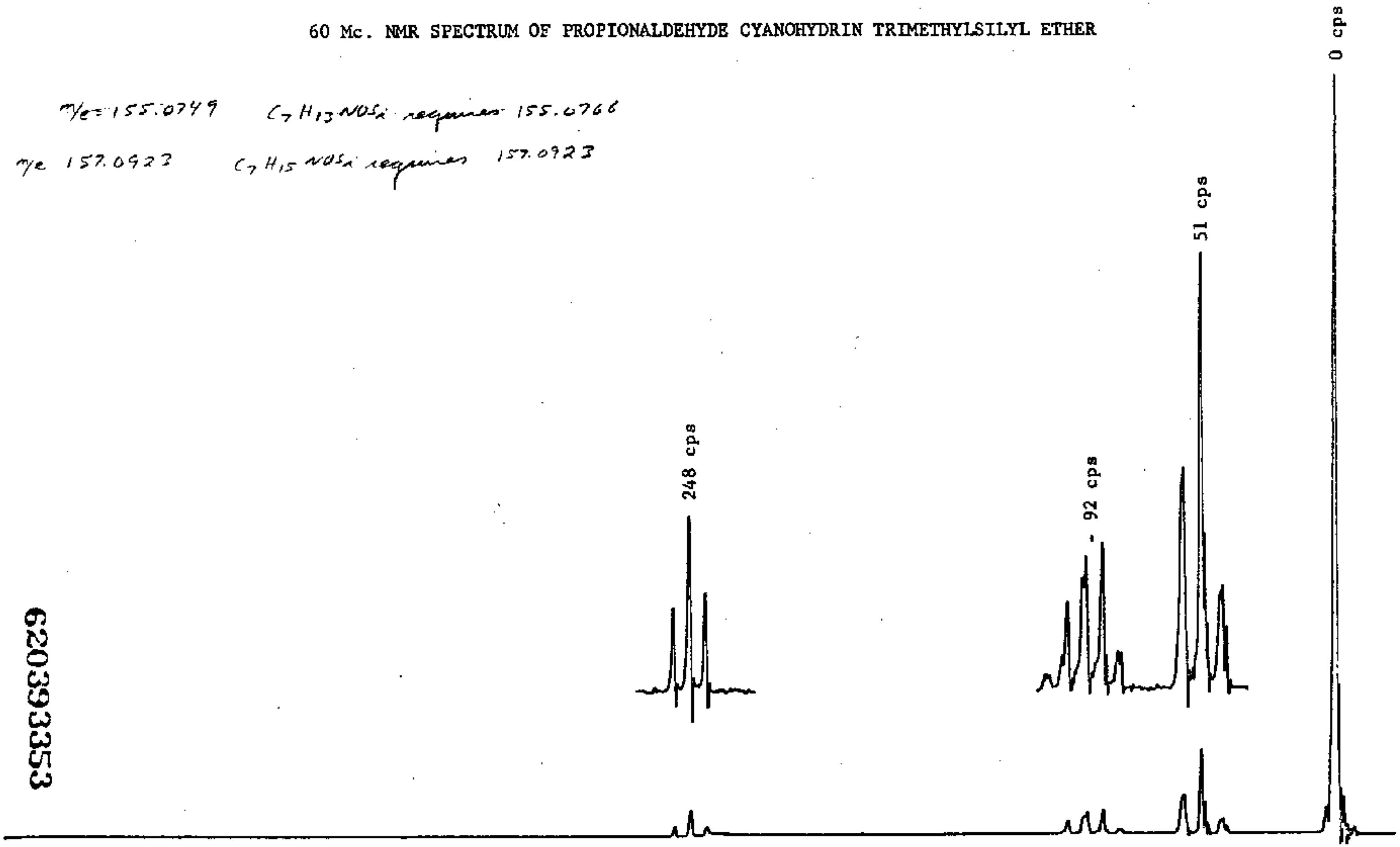


FIGURE 2

60 Mc. NMR SPECTRUM OF PROPIONALDEHYDE CYANOHYDRIN TRIMETHYLSILYL ETHER



m/e = 155.0749 $C_7H_{13}NOSi$ requires 155.0766

m/e 157.0923 $C_7H_{15}NOSi$ requires 157.0923

FIGURE 3

60 Mc. NMR SPECTRUM OF ISOBUTYRALDEHYDE CYANOHYDRIN TRIMETHYLSILYL ETHER

m/e = 171.1136 $C_8H_{17}NOSi$ requires 171.1079

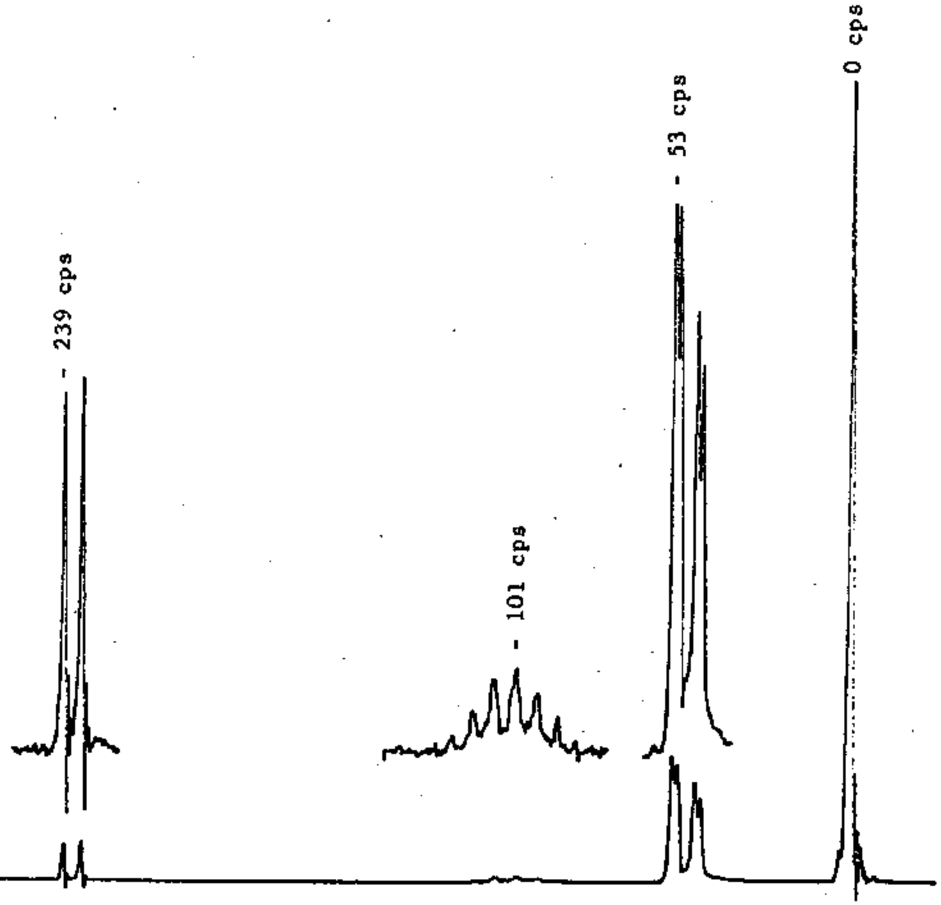


FIGURE 4

60 Mc. NMR SPECTRUM OF ACROLEIN CYANOHYDRIN TRIMETHYLSILYL ETHER

m/e = 155.0749 $C_7H_{13}NOSi$ requires 155.0766