

CASE REPORT

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Cyclohexyl Nitrite Encounter

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ABSTRACT: A brown glass bottle containing yellow liquid was submitted for examination for the presence of common controlled substances. While no controlled substances were detected, the liquid was identified as impure cyclohexyl nitrite, a compound of the same chemical class as amyl and butyl nitrite, which are known for their abuse potential. A bottle labeled cyclohexyl nitrite, but not confirmed by analysis, is the only known previous case submitted to this lab. The case history, examination, and analytical results are presented.

KEYWORDS: forensic science, drugs, inhalants, substance abuse detection, nitrites, cyclohexyl nitrite

A brown glass bottle was reportedly found in the pocket of a transient male arrested for assault. The suspect claimed the unlabeled bottle was video cassette recorder (VCR) tape head cleaner. Police submitted the bottle to the crime lab to analyze the contents for the presence of common controlled substances. No controlled substances were detected in the yellow, transparent liquid found inside the bottle. A vapor phase infrared spectrum (Fig. 1) indicated a nonaromatic, fairly simple nitrite, distinguishable from the more frequently abused amyl, iso-amyl, and butyl nitrites. Analysis of the neat liquid and its headspace vapors by gas chromatography-mass spectrometry indicated a cyclohexanol (Fig. 2, structure I) moiety. Capillary gas chromatography-FID indicated a molecule of similar volatility to ethylbenzene, and slightly less volatile than cyclohexanol. A literature search for cyclohexyl nitrite (Fig. 2, structure II) revealed very little information, and no evidence of its use as a video head cleaner. Several local VCR repair and service shops were contacted and none had ever heard of or knew of any use for cyclohexyl nitrite. Liquid video head cleaners were all reported to be alcohol based.

Methods and Materials

A cyclohexyl nitrite standard was prepared in the author's laboratory by reacting cyclohexanol with potassium nitrite in sulfuric acid. The yellow liquid and synthesized standard were examined as follows.

Fourier transform infrared spectrophotometry was performed on a Digilab Bio-Rad Model FTS-7 equipped with potassium bromide

optics and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. Both the neat liquid on a salt plate and the room temperature vapors from the liquid were sampled.

Gas chromatography-mass spectrometry (GC-MS) data were obtained using a Hewlett Packard 5890 Series II gas chromatograph equipped with a 30 m fused silica capillary column of 0.25 mm inside diameter and an HP-5 (DB-5) film thickness of 0.25 μm . Interfaced with the gas chromatograph was a Hewlett Packard 5972 Mass Selective Detector operated under electron impact ionization at 70 eV (full-scan mode). Room temperature headspace vapors were examined using a temperature program beginning at 40°C, held for 2 min, ramped 8°C per min to 260°C and held there for 5.5 min. Samples were run neat and diluted with methylene chloride.

A Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector was additionally employed for analysis of the liquid's heated headspace vapors. A small quantity of the liquid was placed in a quarter-pint metal can and sealed with a vapor-tight friction lid. The can was heated approximately 30 min at 85°C. Approximately 500 μL of the can's headspace vapors were sampled with an airtight syringe and injected onto the gas chromatograph. A fused silica 60 m capillary column, 0.25 mm inside diameter, 1 μm DB-1 film thickness, was used. The initial oven temperature of 35 deg was held for 2 min, then ramped to 260°C at 8°C/min and held for 5 min.

Nuclear magnetic resonance spectrometry (carbon 13 and proton) was obtained and will be published separately.

Results

The analytical data for the evidence sample were consistent with the synthesized cyclohexyl nitrite standard (Figs. 3–10). Variations between the standard and the evidence sample occurred due to the impurity of the case liquid and to gradual degradation of the cyclohexyl nitrite to cyclohexanol, as suggested by gas chromatographic analyses of a vapor-tight can's headspace sampled a month after the initial examination. The original analysis revealed a large first peak followed by a smaller peak having the same retention time as cyclohexanol. A month later the same sample gave a very small initial peak followed by a predominant later peak having the retention time of cyclohexanol; both retention times were the same as those observed a month earlier.

GC-MSD data for the case liquid and for cyclohexyl nitrite both show a larger initial peak followed approximately half a minute later by a smaller peak (Fig. 5) consistent with cyclohexanol. Formation of some cyclohexanol upon injection was not eliminated.

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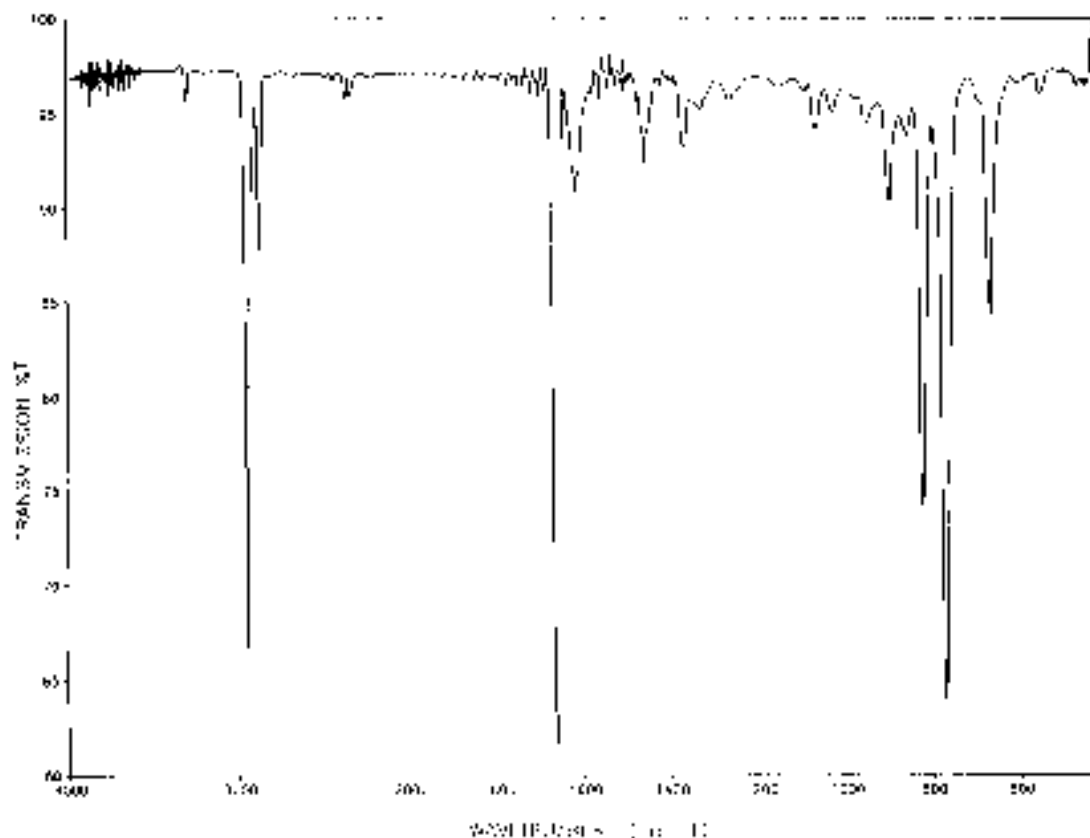


FIG. 1—Room temperature vapor phase infrared spectrum of the case sample liquid. The liquid was placed on a tissue in a cardboard tube, which was placed in the infrared beam path.

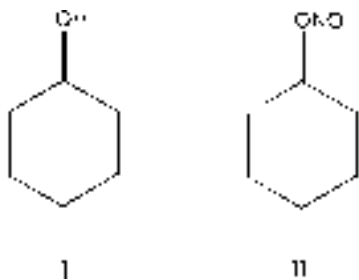


FIG. 2—Structures of cyclohexanol (I) and cyclohexyl nitrite (II).

A commercial source for a cyclohexyl nitrite standard was not found. A mass spectrum was, however, located in a collection of mass spectral data (1). This spectrum was consistent with the mass spectrum shown in Fig. 11, retrieved from the instrument-provided NIST PBM library.

A case submitted approximately two years earlier by the Federal Aviation Association (FAA) involved a box of brown glass bottles labeled as cyclohexyl nitrite. One of the bottles was submitted to this lab, again for the analysis of controlled substances. While no controlled substances were reportedly detected in that sample, characterization and identification of the liquid was not pursued, and it is unknown whether the bottles had been correctly labeled.

Interestingly, the suspect in the FAA case also claimed the liquid was video head cleaner. The investigator later learned that a pornography shop was the destination for the shipment of brown glass

bottles. The FAA investigator and the officer in the assault case, upon mutual agreement, were alerted to each other's investigations.

Discussion

Cyclohexyl nitrite belongs to the same chemical class as amyl and butyl nitrite. Amyl nitrite is a prescribed vasodilator used for the treatment of hypertension and for treating hydrogen cyanide poisonings. It is administered by inhalation, typically from glass ampules (2). Amyl nitrite was abused when users wanted a high or when they felt it would enhance sexual orgasms. Restrictions of this nitrite led to abuse of butyl nitrite, which was available without prescription in over-the-counter commercial products (3). While cyclohexyl nitrite has not been reported to the author's knowledge to be similarly abused, it would appear to be subject to such abuse potential due to its volatility and nitrite functional group. Recent Internet search results on "cyclohexyl nitrite" yielded sites on sexual topics of which the compound was listed, along with amyl, butyl, and isobutyl nitrite, as drugs used for sexual enhancement.

When amyl nitrite is heated, it can emit toxic fumes of nitrogen oxides; it can also react with oxidizing or reducing chemicals (4). In addition, isoamyl nitrite is reportedly capable of forming an explosive mixture with air (5). Cyclohexyl nitrite would be expected to behave similarly.

Since there appears to be no known legitimate commercial or clinical use for cyclohexyl nitrite, this case sample may represent a clandestinely manufactured substance having similar physiological properties as the more commonly known amyl and butyl nitrites.

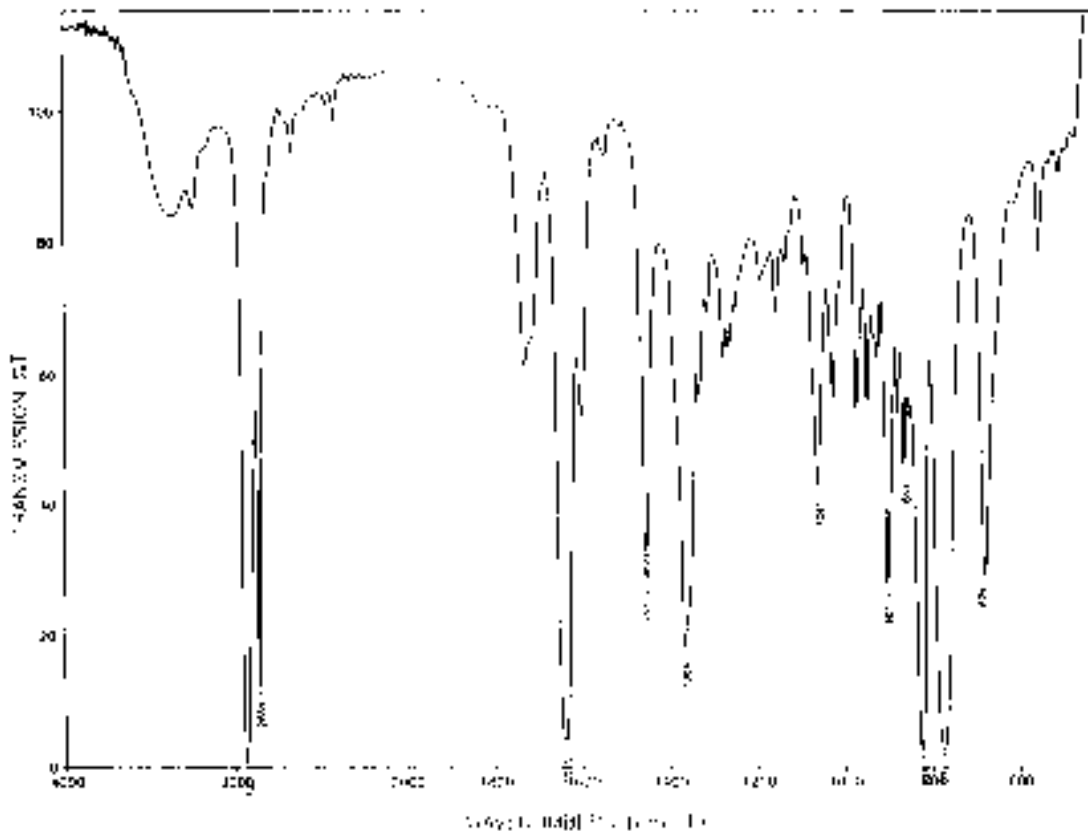


FIG. 3—Infrared spectrum of the neat impure liquid from the case on a salt plate.

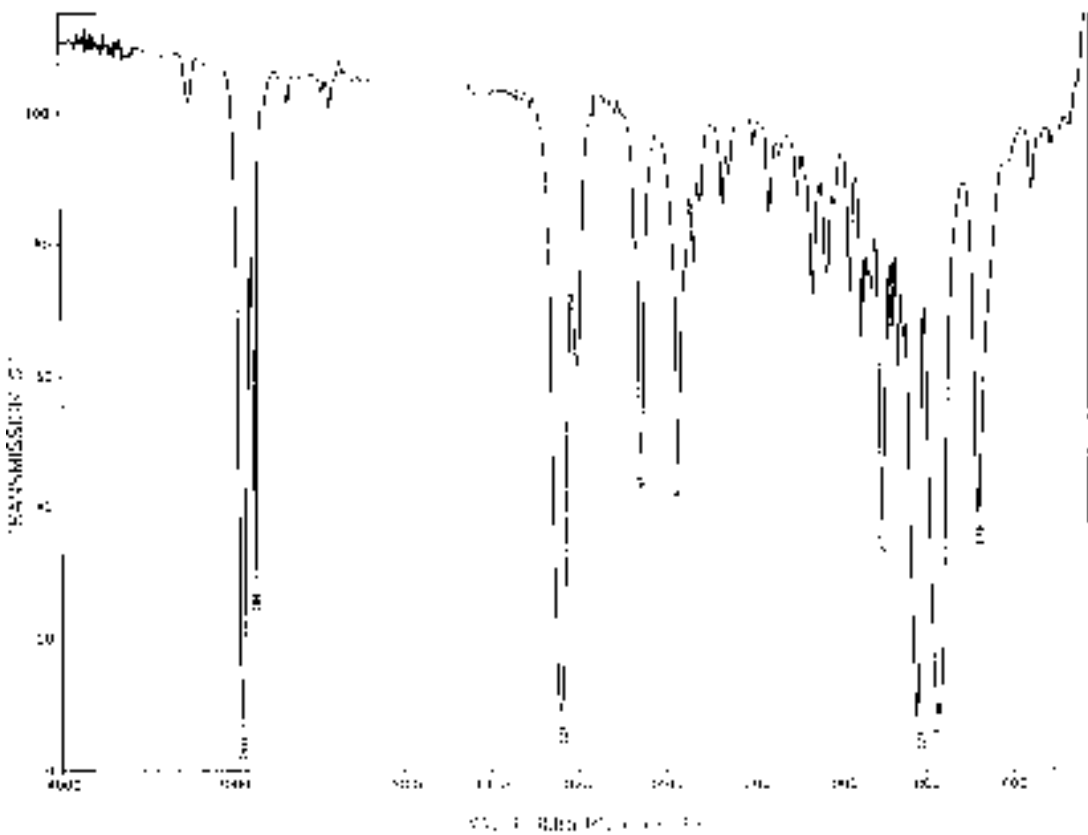


FIG. 4—Infrared spectrum of synthesized cyclohexyl nitrite on a salt plate.

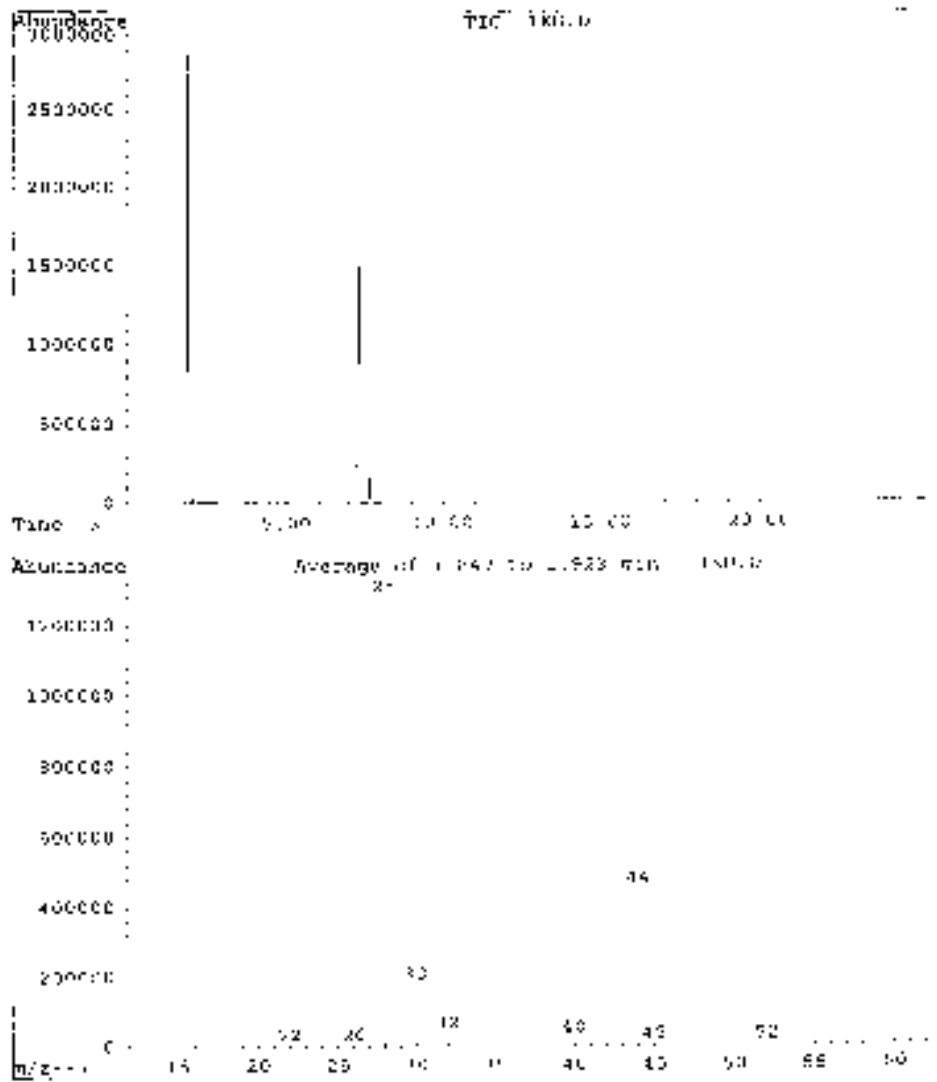


FIG. 5—Total ion chromatogram of the room temperature vapors sampled from the case liquid bottle. The large peak at 1.0 min is air. The mass spectrum of the peak at 7.2 min is shown in Fig. 6 and is consistent with cyclohexyl nitrite. The small peak at 7.6 min is consistent with cyclohexanol (see Fig. 7 for the mass spectrum).

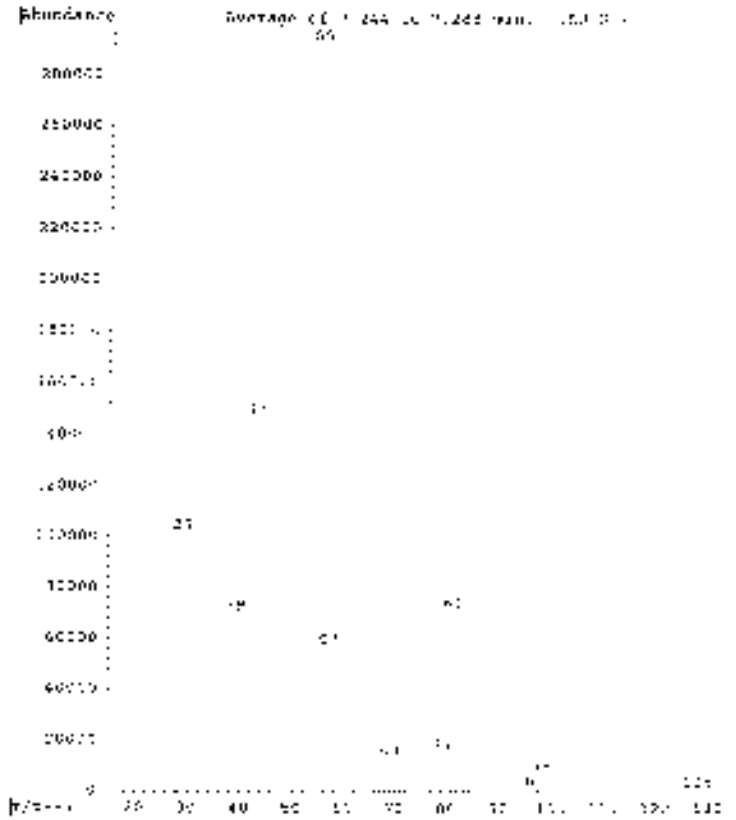


FIG. 6—Mass spectrum of the case sample's peak eluting at 7.2 min. This peak is consistent with cyclohexyl nitrite.

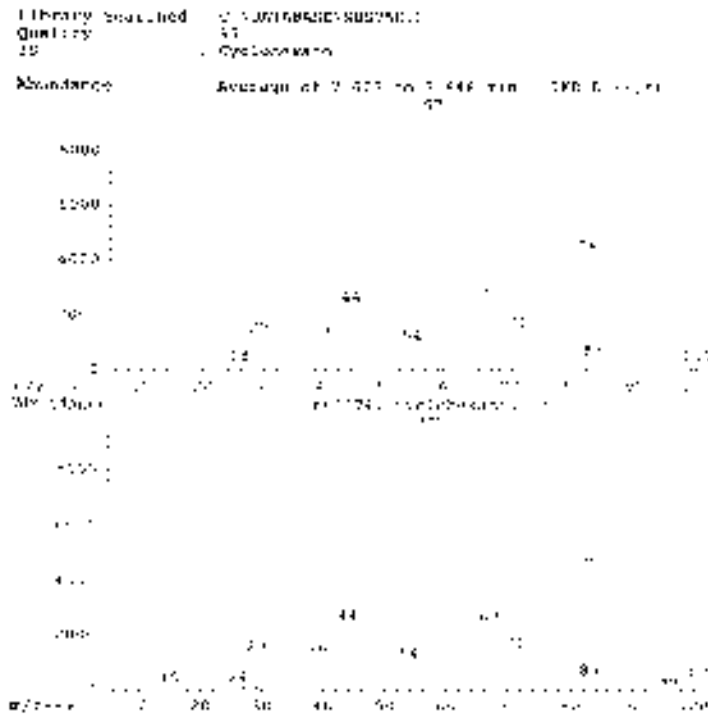


FIG. 7—Mass spectrum of the case sample's smaller peak with the library search result of cyclohexanol shown below. A commercial source of cyclohexanol was examined and found to give mass spectral results consistent with those shown in the library search.

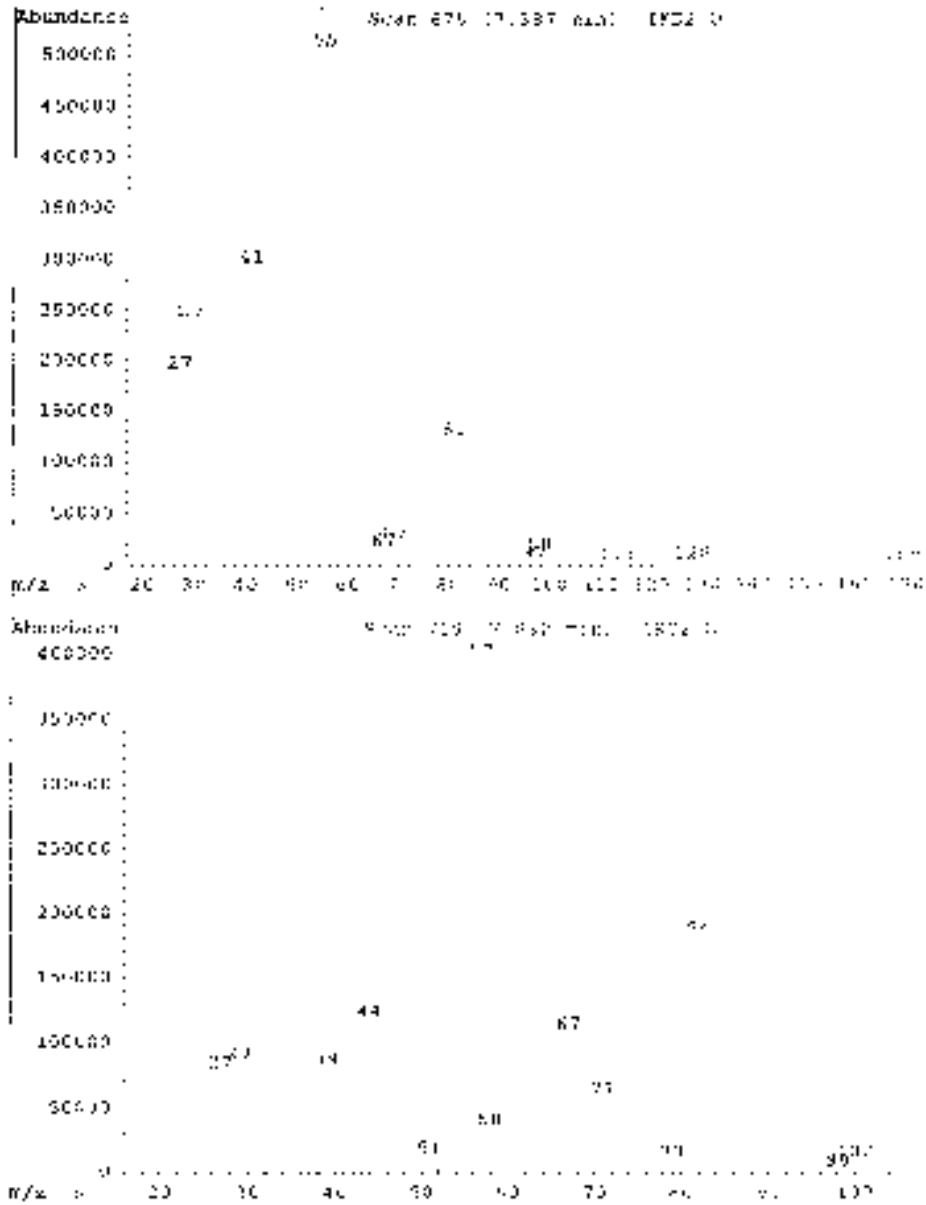


FIG. 8—Mass spectra of the case liquid's two predominant peaks when injected as a liquid diluted with methylene chloride. Note the slightly longer retention times. This is not significant given the manual injections, broader peak widths and larger sample size with the liquid injection.

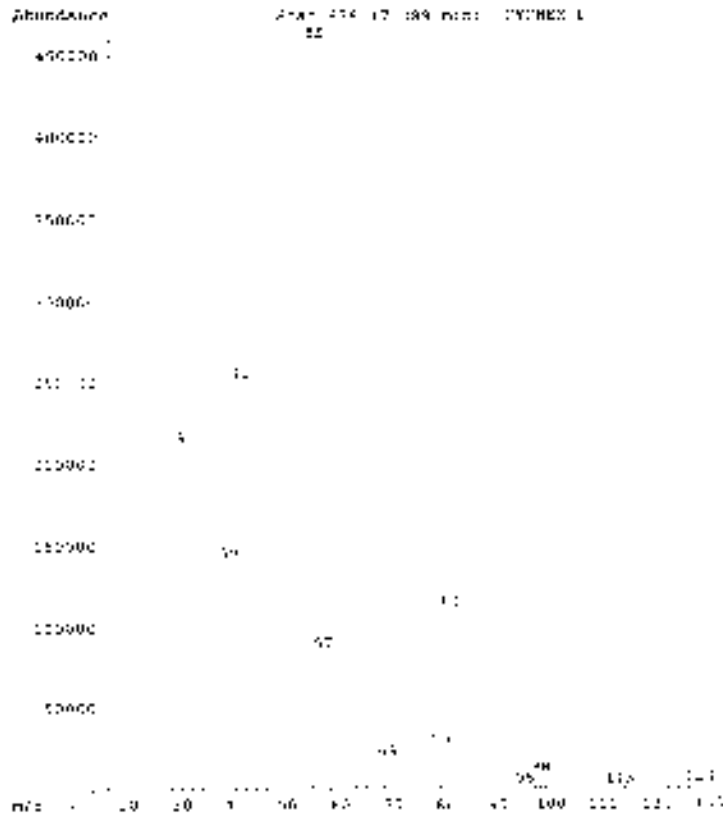


FIG. 9—Mass spectrum of the prepared cyclohexyl nitrite; injection is diluted with methylene chloride. The total ion chromatogram is not shown, but is consistent with that of Fig. 5.

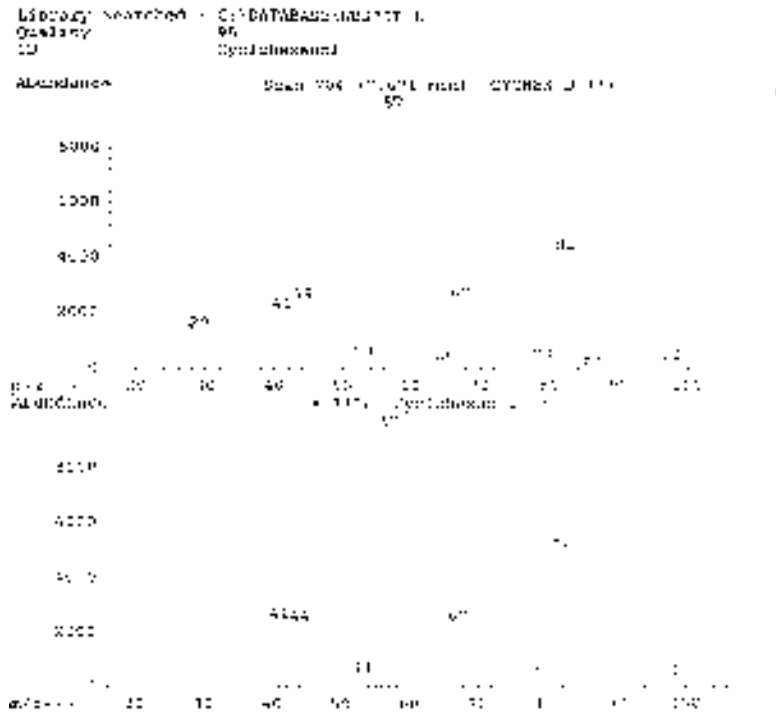


FIG. 10—Mass spectrum of the smaller peak following the major peak of cyclohexyl nitrite; injection as in Fig. 9. The library search result is shown below.

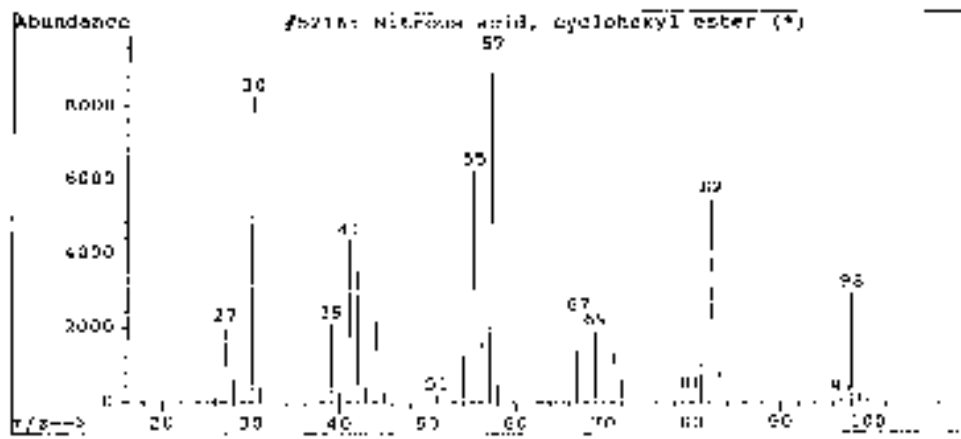


FIG. 11—Mass spectrum of cyclohexyl nitrite retrieved from instrument-provided library.

The decreased availability of the latter may have initiated this development. However, it is unknown why a chemist would choose to synthesize a seemingly novel compound rather than amyl or butyl nitrite, the syntheses of which are a fairly straightforward reaction between a nitrite salt and the parent alcohol.

Acknowledgments

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