constant depending on the rate of loss of residue, and C and t are as previously defined.

Applying a linear regression to the data in Table II for MB residues at 2 h after fumigation gives a correlation coefficient of 0.99997, which indicates excellent linearity of residue vs. applied dose. However, the line obtained does not pass through the origin, and consequently the residue is only approximately proportional to the applied dose.

LITERATURE CITED

Benschoter, C. A. *J. Econ. Entomol.* **1979**, *72*, 401.
Berck, B. *J. Chromatogr. Sci.* **1975**, *13*, 256.
Daniels, F.; Alberty, R. A. "Physical Chemistry"; Wiley: New York, 1956; pp 199, 200.
Dennis, N. M.; Eason, G.; Gillenwater, H. B. *J. Econ. Entomol.* **1972**, *65*, 1753.
Environmental Protection Agency *Fed. Regist.* **1977**, *42* (240), 63134–63161.
Hartsell, P. L., USDA-SEA-AR, Stored-Products Insects Research Laboratory, Fresno, CA 93727, personal communication, 1980.
Heuser, S. G.; Scudamore, K. A. *J. Sci. Food Agric.* **1969**, *20*, 566.
King, J. R., USDA-SEA-AR, Subtropical Horticulture Research Station, Miami, FL 33158, unpublished data, 1980.
King, J. R.; von Windeguth, D. L.; Burditt, A. K., Jr. *J. Agric. Food Chem.* **1980**, *28*, 1049.
Malone, B. *Residue Rev.* **1971**, *38*, 21.
Scudamore, K. A.; Heuser, S. G. *Pestic. Sci.* **1970**, *1*, 14.

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Photohydrolysis of Methyl Bromide and Chloropicrin

Charles E. Castro* and Nao O. Belser

The rate of hydrolysis of methyl bromide and chloropicrin can be markedly enhanced by light. An ~7-fold increase in the rate for methyl bromide results from irradiation with a small pen-ray UV lamp (k_λ = 2.0×10^{-6} s^{-1}). At least 99.6% of the reaction proceeds quantitatively to methanol, bromide ion, and protons. A trace of methane (<0.4%) is produced. The lack of any significant oxidation product of methanol or bromide ion along with the very small yield of methane is interpreted to indicate the reaction is the result of the direct hydrolysis of photoexcited methyl bromide. Chloropicrin is decomposed even more rapidly by light ($k_\lambda = 1.4 \times 10^{-4}$ s^{-1}). In neutral aqueous solution without irradiation, no hydrolysis is detected in 10 days. With irradiation, a 10^{-3} M solution is dissipated in hours. The products of the aqueous photo reaction in air are carbon dioxide, chloride ion, nitrate ion, and protons. Nitrite ion can be detected in small amounts (~2–3%) when the reaction is conducted under argon. The nitrite to nitrate conversion is *not* fast enough to accommodate the kinetics under aerobic conditions.

Methyl bromide mixed with chloropicrin is a widely used combination for preplant soil sterilization. While the volatility of these halides suggests that significant amounts of them would escape the soil matrix, very little is known of their actual environmental chemistry.

In the course of our general studies of the microbiological and chemical transformations that haloorganic biocides may undergo [for summaries, cf. Castro (1977) and Castro et al. (1978)], we have learned that the hydrolysis of methyl bromide and chloropicrin can be markedly enhanced by light. The results show that photohydrolysis can be an important means of environmental detoxification for substances of this class.

EXPERIMENTAL SECTION

Materials and Methods. Chloropicrin, Eastman White Label, and methyl bromide, Matheson, were used without purification. Flame ionization gas chromatographic analysis of methyl bromide, chloropicrin, methanol, and methane was accomplished with a Varian 2440 gas chromatograph by direct injection of the aqueous solution and gas phase. The columns employed were all $^1/_8$ in. i.d. Porapak P columns of varying length: methyl bromide and methanol (18 in.; 160 °C), methane (6 ft; 100 °C), and chloropicrin (6 in.; 120 °C). Except for methane, quantitation of these substances was accomplished by sequential injection of reaction mixture and known amounts of standard. Calibration curves constructed from analysis of solutions of known composition of one of the above and standard were identical with those obtained by sequential injection of the components. The sequential injection procedure was then used to eliminate the complexities associated with the reaction of the standards during photolysis. The standards employed were 1-butanol, for chloropicrin, and acetone, for methyl bromide and methanol. Methane was quantitated by spiking with known amounts of methane. Reproducibility was ±7% in all cases. Chloride and bromide ions were determined by direct potentiometry employing Orion specific ion electrodes and a calomel reference electrode (Castro and Bartnicki, 1965; Castro and Belser, 1966). Nitrate ion was assayed by nitrating toluene and determining the amount of nitrotoluene in toluene by the absorption spectrum of the molecular complex (Bhatty and Townshend, 1971). Nitrite was determined in two ways: by using the above procedure, with a prior oxidation to nitrate and by diazotization and coupling of sulfanilic acid with *N*-(1-naphthyl)ethylenediamine (Feinsilver and Oberst, 1953).

Carbon dioxide was qualitatively established as the only gaseous product by mass spectrometric analysis of the gas produced by a photolysis of chloropicrin in water run in an argon atmosphere. In addition, a run with $Cl_3C^{14}NO_2$ (the synthesis will be reported elsewhere) yielded $BaC^{14}O_3$

Department of Nematology, University of California, Riverside, Riverside, California 92521.

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upon treatment of the product solution with barium hydroxide. For quantitation, carbon dioxide was determined gravimetrically as barium carbonate. The gas phase in the reactor was passed with argon through a trap of barium hydroxide. An aliquot of the solution was directly injected into barium hydroxide. Chloropicrin blanks *did not* precipitate barium carbonate under these conditions.

Photolysis. A typical photolysis of a 10^{-2} M aqueous solution of chloropicrin is described. A tube-shaped photoreactor equipped with stopcocks for argon inlet and outlet (the latter serum capped for gas removal), a manometer, a serum-capped stopcock for solution removal, and a magnetic stirring bar was charged with 100 mL of water and 100 μL (10^{-3} mol) of chloropicrin. The free gas space was 115 mL. The solution was irradiated by a small "pen-ray" low-pressure quartz lamp at 254 nm (Ultraviolet Products, Inc.). The lamp was placed into a vacuum-jacketed quartz finger that slipped into the center of the tube reactor and was sealed by a large ground-glass joint. The top of the lamp was well beneath the surface of the solution. The entire apparatus was immersed in a water bath at 25 °C. Irradiation for 24 h indicated a pressure change of 51 mmHg. A gas sample injected on the Porapak column showed no chloropicrin. The gas phase was then gently blown with argon through a barium hydroxide trap. Aliquots of the solution were removed for chloride, nitrate, nitrite, carbon dioxide, and chloropicrin analysis. At this point the consumption of chloropicrin was complete. Analysis yielded 3.0×10^{-3} mol of Cl^- along with CO_2 (gas and solution), 0.97×10^{-3} mol, nitrate, 1.05×10^{-3} mol, and no nitrite. Under anaerobic conditions, small yields of nitrite (2–3%) could be detected. The yield of nitrate plus nitrite was quantitative. For kinetics, aliquots were directly removed from the solution for chloride and chloropicrin analysis.

Sunlight irradiation was accomplished in a quartz spectrophotometric cuvette, fitted with a serum-capped stopcock. The cuvette was exposed to sun for 2 full days in August. Flood lamp irradiation was accomplished with a 150-W lamp. The reaction was conducted in a Pyrex round-bottom flask suitably equipped.

The methyl bromide hydrolyses were conducted in completely filled glass-stoppered, 10-mL volumetric flasks. Each was charged with an aliquot of the same 10^{-2} M stock solution.

The photohydrolysis of this substance was conducted in a manner similar to that of chloropicrin. In one of the product runs, a 5-L flask was charged with 4980 mL of 1.65×10^{-2} M methyl bromide solution. Irradiation with the same pen-ray lamp in the same quartz finger (described above for chloropicrin) for 40 days yielded a solution that was $(1.5 \pm 0.1) \times 10^{-2}$ M in methanol and 1.6×10^{-2} M in bromide ion. A trace of methane, 0.4%, was detected in the gas phase.

RESULTS AND DISCUSSION

Methyl bromide hydrolyzes quite slowly at neutral pH in laboratory light to methanol, bromide, and hydrogen ion (eq 1).

$$CH_3Br + H_2O \xrightarrow{k_1} CH_3OH + H^+ + Br^- \quad (1)$$

The rate for the process, monitored by following H^+, was established some time ago by Moelwyn-Hughes (1938, 1949). Utilizing gas chromatography for methyl bromide and methanol and direct potentiometry for bromide ion (Castro and Bartnicki, 1965), we have followed all three species for both the normal and photohydrolysis.

First-order plots for the disappearance of methyl bromide and the appearance of methanol (or Br^-) are shown in Figure 1. Bromide and methanol follow the same slope. Thus, experimentally

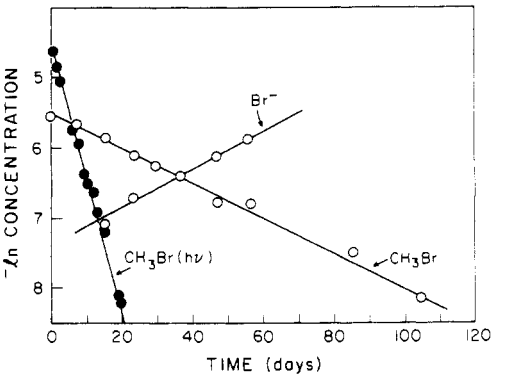

Figure 1. First-order plots for the rates of methyl bromide hydrolysis, showing disappearance of methyl bromide (CH_3Br), appearance of bromide ion (Br^-), and the rate of methyl bromide decay upon illumination at 254 nm [CH_3Br ($h\nu$)].

$$\frac{-d(CH_3Br)}{dt} = \frac{d(CH_3OH)}{dt} = \frac{d(Br^-)}{dt} = k_1(CH_3Br) \quad (2)$$

The rate constant obtained from repeated runs for all three species is $k_1 = (3.0 \pm 0.1) \times 10^{-7}$ s^{-1}. This is in good agreement with the value (3.0×10^{-7} s^{-1}) found by Moelwyn-Hughes at pH 7.0.

Photohydrolysis. Illumination of an aqueous methyl bromide solution at 25 °C resulted in a marked increase in the rate of hydrolysis. The first-order plot for methyl bromide disappearance under these conditions is also shown in Figure 1. The rate constant for the hydrolysis catalyzed by the pen-ray lamp is $k_\lambda = (2.0 \pm 0.1) \times 10^{-6}$ s^{-1} and represents a 6.6-fold increase. It should be emphasized that photolysis *does not* alter either the stoichiometry (eq 1) or the general rate law (eq 2). That is, monitoring methyl bromide, methanol, and bromide ion with time demonstrated eq 2 was valid and yielded the same rate constant for all species within experimental error (±7%).

A search was made for other products that might be indicative of an initial free radical scission (eq 3):

$$CH_3Br \xrightarrow{h\nu} CH_3\cdot + Br\cdot \quad (3)$$

A very small amount of methane could be reproducibly detected in the photolytic runs, but it accounted for less than 0.4% of the product. Moreover, products of methyl bromide oxidation (acetaldehyde; acetic acid) were not detectable nor were any inorganic oxidants (e.g., BrO_3^-). There were no oxidants in the product solution (no oxidation of acidic potassium iodide).

We conclude that except for a very minute fraction of the reaction homolysis, process 3, is unimportant. The almost exclusive path of decay (>99.6%) represents the direct hydrolysis of photoactivated methyl bromide:

$$CH_3Br \xrightarrow{h\nu} (CH_3Br)^* \xrightarrow{H_2O} CH_3OH + H^+ + Br^- \quad (4)$$

In contrast to the slow normal hydrolysis of methyl bromide, at pH 7, we detect almost no hydrolysis at all of chloropicrin after several weeks. A 10^{-2} M solution of chloropicrin stored in the dark yielded at most $<8 \times 10^{-5}$ M chloride ion in 56 days. This would correspond to a maximum rate constant of $\sim 2 \times 10^{-9}$ s^{-1}. However, the influence of light upon the reaction is dramatic.

The rate of disappearance of chloropicrin under four conditions of illumination (cf. Experimental Section) is shown in Figure 2. The actual rates reflect the amount of light received by the sample in the blue-UV region

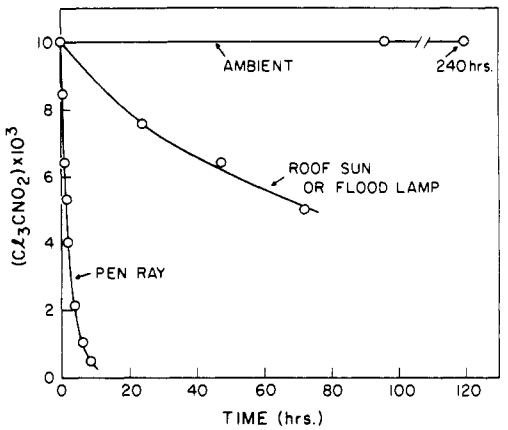

Figure 2. Rates of decay of chloropicrin in water with ambient light, roof sunlight or a flood lamp, and UV irradiation.

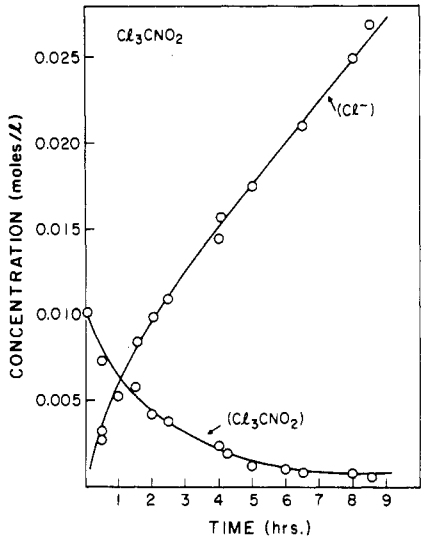

Figure 3. Rates of photohydrolysis of chloropicrin showing chloropicrin consumption (Cl_3CNO_2) and chloride release (Cl^-).

(chloropicrin begins to absorb below 300 nm). The curve for the sunlight experiment and that obtained by flood lamp irradiation (through Pyrex) are the same. Under these conditions $t_{1/2} \simeq 3$ days. The complete dissipation of the substance in 6 h upon pen-ray illumination is in striking contrast to the lethargy to hydrolysis in ambient light. Under these conditions $k_\lambda = 1.39 \times 10^{-4}$ s^{-1} and represents a 10^4–10^5 rate enhancement.

The fact that the hydrolysis of chloropicrin is hastened by light was noted in the old literature (see below). However, the nature of the process or the degree of enhancement has never been established. Gas-phase studies by Steacie and Smith (1938) and later by Ashmore and Norrish (1951) established that chloropicrin can be photolytically decomposed to phosgene and nitrosyl chloride:

$$Cl_3CNO_2\ (g) \xrightarrow[\text{or } \Delta]{h\nu} Cl_2CO + NOCl \qquad (5)$$

Thermolysis (Dubikhin et al., 1971) proceeds analogously. As with methyl bromide, we have monitored the rates in aqueous solutions by following both chloride appearance and chloropicrin decay (Figure 3). It will be noted from the concentration vs. time plots of Figure 3 that chloride is not produced at a rate equal to 3 times that of chloropicrin disappearance. Thus, there are chlorinated intermediates produced in the process. The overall stoichiometry we observe for the photolysis in air is given by

$$Cl_3CNO_2 \xrightarrow[H_2O]{h\nu} 3Cl^- + CO_2 + NO_3^- + 4H^+ \qquad (6)$$

Alekseevskii (1933) was the first to observe that the decomposition of chloropicrin in aqueous solution could be enhanced by light. He noted that X-rays, a photovoltaic discharge, a mercury lamp and charcoal containing 1% sodium hydroxide promoted the decomposition—with the latter being most effective. He formulated these processes as a decomposition to phosgene and nitrosyl chloride (eq 5), followed by hydrolysis of these substances to carbonate and nitrous acid.

Actually, the light- and base-catalyzed reactions represent different processes. Chloropicrin is quite susceptible to nucleophilic attack, and alkoxide (Jacobs, 1949; von Hartel, 1927), sodium peroxide (Feinsilver and Oberst, 1953), and iodide (Jacobs, 1949) have all been employed in an attempt to fully liberate nitrite from chloropicrin. The presumed stoichiometry with iodide, for example, is given in eq 7. While it is true that tetraiodomethane is

$$4I^- + Cl_3CNO_2 \rightarrow CI_4 + 3Cl^- + NO_2 \qquad (7)$$

produced from the reaction (Kretov and Melnikov, 1933), it is by no means established that the reaction proceeds quantitatively as written. In fact, several products, including carbon monoxide, have been observed. Correspondingly, ortho esters are obtained from reactions of alkoxides with chloropicrin (von Hartel, 1927) (eq 8) along

$$4CH_3O^- + Cl_3CNO_2 \rightarrow (CH_3O)_4C + 3Cl^- + NO_2^- \qquad (8)$$

with carbonate esters and other products, but it was not established that the reaction was quantitative. Feinsilver and Oberst (1953) found in their studies of these reactions that only refluxing with sodium peroxide in aqueous alcohol reproducibly and quantitatively liberated nitrite ion. A subsequent assay for nitrite provides the basis for a quantitative microdetermination of chloropicrin. Other products from the reaction were not characterized but were presumed to be chloride and carbonate ions.

Under aerobic conditions, we find nitrate but not nitrite as the *only* observable nitrogenous product from the aqueous photolysis. The stoichiometry as written in eq 6 is quantitative for all products within experimental error. On the other hand, if the reaction is carried out in an argon-purged aqueous solution under an argon atmosphere, some nitrite is detectable. Thus, photolysis of a 10^{-3} M aqueous solution of chloropicrin under these conditions, stopped at 5 h, yielded chloropicrin (3.3×10^{-3} mol, 33% remaining, 67% conversion), chloride ion (2.0×10^{-3} mol, 100%), nitrate ion (6.3×10^{-4} mol, 94%), carbon dioxide (6.6×10^{-4} mol, 99%), and nitrite ion (0.35×10^{-4} mol, 5.2%). Nitrite is oxidized to nitrate in acidic solution, but the process is too slow to accommodate our findings. Thus, photolysis of a 10^{-3} M solution of sodium nitrite in air at pH *1.5* contained 10% of unreacted nitrite after 24 h. No nitrite is obtained from chloropicrin under these conditions, and the reaction solution is much less acidic to begin with. Similarly, bubbling nitrosyl chloride with air slowly through irradiated water did not result in a clean conversion to nitrate. The products are chloride and a corresponding even distribution of nitrite and nitrate. This result and the relatively slow conversion of nitrite to nitrate under reaction conditions eliminate nitrosyl chloride as the major precursor to nitrate in the chloropicrin aqueous photodecomposition. The kinetics of the chloride release and chloropicrin decay, however (Figure 3), clearly require the presence of chlorinated intermediates. The nature of the initial scission in water bears further scrutiny.

The fact that relatively inert alkyl halides like methyl bromide can be induced to photohydrolyze suggests that many other simple compounds of this class (e.g., ethylene dibromide, 1,2-dibromo-3-chloropropane, and 1,3-di-

chloropropene) could be dissipated in the environment with proper exposure to sunlight.

LITERATURE CITED

Alekseevskii, E. V. *J. Gen. Chem. USSR* **1932**, *2*, 341; *Chem. Abstr.* **1933**, *27*, 231.
Ashmore, P. G.; Norrish, G. W. *Proc. R. Soc. London, Ser. A* **1951**, *204*, 34.
Bhatty, M. K.; Townshend, A. *Anal. Chim. Acta* **1971**, *56*, 55.
Castro, C. E. *EHP, Environ. Health Perspect.* **1977**, *21*, 279.
Castro, C. E.; Bartnicki, E. W. *Biochim. Biophys. Acta* **1965**, *100*, 384.
Castro, C. E.; Bartnicki, E. W.; Belser, N. O. *Biochemistry* **1978**, *17*, 5582.
Castro, C. E.; Belser, N. O. *J. Agric. Food Chem.* **1966**, *14*, 69.
Dubikhin, V. V.; Nazin, G. M.; and Manelis, G. B. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, *No. 6*, 1338; *Chem. Abstr.* **1971**, *75*, 75871s.
Feinsilver, L.; Oberst, F. W. *Anal. Chem.* **1953**, *25*, 820.
Jacobs, M. B. "Analytical Chemistry of Industrial Poisons, Hazards and Solvents", 2nd ed.; Interscience: New York, 1949; p 734.
Kretov, A. E.; Melnikov, N. M. *J. Gen. Chem. USSR* **1932**, *2*, 202; *Chem. Abstr.* **1933**, *27*, 952.
Moelwyn-Hughes, E. A. *Proc. R. Soc. London, Ser. A* **1938**, *164*, 300, 302.
Moelwyn-Hughes, E. A. *Proc. R. Soc. London, Ser. A* **1949**, *196*, 542.
Steacie, E. W. R.; Smith, W. M. F. *J. Chem. Phys.* **1938**, *6*, 148.
von Hartel, H. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 1841.

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Identification of a Nonenylnitrolic Acid in Corn Treated with Nitrous Acid

Thomsen J. Hansen,[1] Steven R. Tannenbaum, and Michael C. Archer*[2]

We have previously identified nitrohexane as a major product formed following treatment of corn (*Zea mays*) with nitrous acid. We report here isolation of another compound from nitrosated corn which is an unsaturated nine-carbon nitrolic acid. This nitrolic acid behaves in a similar manner to *N*-nitroso compounds when subjected to various chemical tests which have been used to distinguish *N*-nitroso compounds from other compounds which respond to chemiluminescence detection.

It is well established that the mammalian stomach provides a suitable environment for this formation of *N*-nitroso compounds (Sander et al., 1968; Sen et al., 1969; Mysliwy et al., 1974). Precursors of *N*-nitroso compounds enter the stomach in the form of nitrite from saliva (Tannenbaum et al., 1974, 1976; Spiegelhalder et al., 1976) and nitrite and organic nitrogen compounds, particularly secondary and tertiary amines, in food material. Determination of compounds that form by deliberate nitrosation of food material in vitro may provide an indication of the kinds of compounds that could form in the gastric environment. We have begun to work in this area by investigating the nitrosation of corn. Nitroso compound formation in foods of plant origin has not received much attention. We are also interested in the etiology of gastric cancer in southern Colombia (Correa et al., 1975; Cuello et al., 1976). In this region both intake of nitrate and consumption of corn have a positive association with risk for the disease (Cuello et al., 1976; Tannenbaum et al., 1979).

We have previously reported the identification of nitrohexane as a major product following treatment of corn with nitrous acid (Hansen et al., 1979a). The nitrohexane was identified during our search for nitroso compounds using the thermal energy analyzer (TEA; Fine et al., 1975). During the course of this study, we investigated several other classes of compounds that give positive response on the TEA (Hansen et al., 1979b). We therefore developed procedures to distinguish these compounds from *N*-nitroso compounds that were the main objective of our study (Hansen et al., 1979b).

Using these new methods, however, we have again isolated a TEA-responsive compound in nitrosated corn which is not an *N*-nitroso compound. The isolation and identification of this compound, a nonenylnitrolic acid, which behaved in all the tests like a nitrosamine, is described here.

EXPERIMENTAL SECTION

Materials. Yellow corn was obtained from a region of Nariño in Colombia which has a high incidence of gastric cancer. All solvents were either pesticide grade (Mallinckrodt, St. Louis, MO) or HPLC grade (Fisher, Pittsburgh, PA). Ethylnitrolic acid and hexylnitrolic acid were prepared by nitrosation of nitroethane and nitrohexane, respectively (Smith, 1965). 3-Nonenylnitrolic acid (1-nitro-3-nonenal oxime) was prepared in a three-step synthesis from 1-octen-3-ol as shown in Figure 1.

1-Octen-3-ol (10 g, 78 mmol) was first converted to 1-chloro-2-octene by reaction with 9.2 g (82 mmol) of thionyl chloride in 150 mL of diethyl ether at room temperature overnight (DeWolfe and Young, 1956). The reaction mixture was distilled at aspirator pressure to yield ~8 g (75%) of chlorooctene as a yellow oil (bp 60 °C): NMR ($CDCl_3$) δ 0.9 (t, 3, CH_3), 1.1–1.4 (m, 6, CH_3), 2.0–2.2 (m, 2, CH_2C=), 4.0, 4.1 (d, 2, CH_2Cl), 5.6–5.9 (m, 2, CH=CH). The NMR indicated that the 1-chloro-2-octene was contaminated with ~10% of the isomeric 3-chloro-1-octene.

The chlorooctene (4 g, 27 mmol) was reacted with nitromethane (1.65 g, 27 mmol) in refluxing acetonitrile for

Department of Nutrition and Food Science, Massachusetts Institute of Technology, Cambridge, Masschusetts 02139.
[1]Present address: Laboratory of Carcinogen Metabolism, National Cancer Institute, Bethesda, MD 20205.
[2]Present address: Department of Medical Biophysics, University of Toronto, Toronto, Ontario, Canada M4X 1K9.

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