the methoxy ester (XIII) (13.6 grams, 0.07 mole) and 126.4 grams of a 25% aqueous solution of dimethylamine (0.7 mole) were stirred for 12 hours in a sealed flask at 25°. The water and dimethylamine were then removed under vacuum. The residual yellow oil was dissolved in chloroform and dried over magnesium sulfate. Removal of solvent and distillation gave 10.3 gram (81.7%) of XII [b.p. 129–30.5° (0.5 mm.); n^{25}_D, 1.5243].

Analysis. Calculated for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.60; H, 6.88. Infrared (capillary film, 0.01 mm.): broad bands centered at 3.42 microns (COOH) and 9.05 microns (COC), sharp band at 5.80 microns (CO).

dl - *m,O* - **Dimethylmandeloyl Chloride (XIV).** Thionyl chloride (13.8 grams, 0.12 mole) was added to XII (15.4 grams, 0.09 mole) at 0° with stirring. The temperature of the reaction mixture was then raised to 25° and it was stirred for 12 hours. The excess thionyl chloride was stripped under vacuum and the product distilled [b.p. 89–90° (0.95 mm.); n^{25}_D, 1.5180; yield, 13.6 grams (76%)].

Analysis. Calculated for $C_{10}H_{11}ClO_2$: Cl, 17.85. Found: Cl, 17.99. Infrared (capillary film, 0.01 mm.): bands at 9.03 microns (COC) and 5.58 microns (CO).

dl - *m,N,N,O* - **Tetramethylmandelamide (III) from the Methoxy Acid Chloride (XIV).** To a solution of anhydrous dimethylamine (11.4 grams, 0.252 mole) in 100 ml. of ether, the methoxy acid chloride (XIV) (12.6 grams, 0.063 mole) was added dropwise with stirring and cooling at 0°. The mixture was stirred for an additional hour and then washed with 40 ml. of salt water. The ether portion was separated and dried over magnesium sulfate. After evaporation of the solvent, the product was distilled [b.p. 108° (0.4 mm.); n^{25}_D, 1.5270; yield, 8.1 grams (61.8%)]. The infrared spectrum (capillary film, 0.01 mm.) was identical with that of a sample of III prepared from the chloro amide (II).

Herbicide Screening Results. The final products (I to IV) and all of the related intermediates except the relatively unstable cyanohydrin and the acid chlorides were evaluated for pre-emergence (seed germination inhibition) and postemergence (foliage spray) herbicidal activity. Representatives of six species of grasses (monocotyledons) and seven species of broadleaf plants (dicotyledons) were employed. The pre-emergent test procedure used has been reported (*4*). Postemergent application was made to 2-week-old foliage of the same group of plant species at desired solution concentrations. Volumes were controlled to give precise rates per acre.

Action of any significance was confined to four of the compounds tested. *N,N*-Dimethyl-2-(*m*-tolyl) acetamide (I) was the most effective pre-emergent herbicide, exhibiting severe inhibition of germination of four grass species and one broadleaf species at rates as low as 5 pounds per acre. The chloro dimethylamide (II) showed activity against several grass and broadleaf species at the rate of 25 pounds per acre.

The methoxy methyl ester (XIII) and the methoxy acid (XII) exhibited pre-emergent activity at 25 pounds per acre with a change in plant specificity. Seeds from representatives of the Cruciferae (mustards) and Chenopodeaceae (lambsquarter) failed to germinate with these two compounds.

Compounds XII and XIII also showed postemergence activity on broadleaf plants, the visual injury being characterized by formative changes of the leaves. Radishes (Crucifereae) were severely injured at rates as low as 4 pounds per acre.

The methoxy dimethylamine (III) and the dimethylamino dimethylamide (IV) were essentially inactive in all tests.

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LABELED CARBAMATES

Synthesis of C^{14}-Labeled 2-Methyl-2-(methylthio)propionaldehyde O-(Methylcarbamoyl)oxime

W. J. BARTLEY, D. L. HEYWOOD, T. E. N. STEELE, and W. J. SKRABA

Union Carbide Corp., South Charleston, W. Va.

DURING THE PAST THREE YEARS, extensive field tests on 2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime—Union Carbide 21149, formulated as a 10% granular under the proposed trademark Temik—have shown this compound to be a very promising broad spectrum systemic insecticide, nematocide, and acaricide (*12, 18*). Its potential use on cotton, tobacco, potatoes, and other crops required a study of its metabolism in both plants and animals. To implement these metabolic studies (*4, 7, 8*), technical Temik was synthesized labeled with C^{14} at three different sites of the molecule. In addition, the corresponding sulfoxide was prepared by oxidation of C^{14}-labeled Temik.

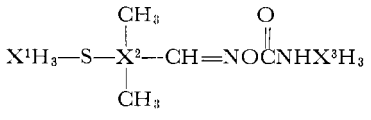
To facilitate discussion, the carbamate insecticide [2-methyl-2-(methylthio)-propionaldehyde *O*-(methylcarbamoyl)-oxime] will be referred to as Temik, the corresponding sulfoxide [2-methyl-2-(methylsulfinyl)propionaldehyde *O*-(methylcarbamoyl)oxime] as Temik sulfoxide and the parent oxime [2-methyl-2-(methylthio)propionaldehyde oxime] as Temik oxime.

Discussion

tert-C^{14} Temik (III) was prepared by the sequence of reactions summarized in Figure 1. The transformations, which are detailed in the experimental section, generally proceeded smoothly as anticipated from preliminary syntheses. However, for unknown reasons, abnormally low yields were obtained in the syntheses of 2-methyl-2-propanol-2-C^{14} and 2-chloro-2-methyl-2-C^{14}-1-nitrosopropane dimer (I) resulting in the loss of considerable radioactivity in these steps. The over-all yield of Temik from barium carbonate-C^{14} was about 4%.

The *S*-methyl-C^{14} Temik (IV) was prepared by reaction of sodium methyl-C^{14}-mercaptide with 2-chloro-2-methyl-1-nitrosopropane dimer (I) followed by reaction with methyl isocyanate. The over-all yield from dimer was 64%.

The synthesis of 2-methyl-2-(methylthio)propionaldehyde O-(methylcarbamoyl)oxime (Temik) with a C^{14} tag at three different sites in the molecule has been accomplished. These were: *S*-methyl-C^{14} Temik, obtained by reaction of methyl-C^{14}-mercaptan with 2-chloro-2-methyl-1-nitrosopropane dimer; *tert*-C^{14} Temik, obtained in an eight-step synthesis starting with tagged barium carbonate; and *N*-methyl-C^{14} Temik resulting from reaction of the appropriate aldehyde oxime with methyl-C^{14} isocyanate. The tagged methyl isocyanate was prepared in good yield by a new method involving reaction of *N,N'*-carbonyldiimidazole and methyl-C^{14}-amine hydrochloride. The *N*-methyl-C^{14} sulfoxide of Temik [2-methyl-2-(methylsulfinyl)propionaldehyde O-(methyl-C^{14}-carbamoyl)oxime] was prepared by peracid oxidation of labeled Temik.



N-methyl-C^{14} Temik (V) was synthesized from methyl-C^{14} isocyanate, which was readily liberated upon heating methyl-C^{14}-amine hydrochloride and *N,N'*-carbonyldiimidazole (VI) under vacuum, as illustrated in Figure 2. The intermediate methylcarbamoyl - 1-imidazol (VII) is not isolated but dissociates readily (*16*) under the reaction conditions to give 75 to 85% yields of high purity methyl-C^{14} isocyanate. This synthesis appears especially adaptable to the preparation of a large variety of either carbonyl-C^{14} or *N*-methyl-C^{14} methylcarbamates and will be the subject of a forthcoming paper (*2*).

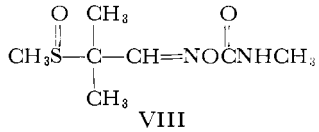
In all instances, the labeled products were shown to have radiochemical purities of 98.5 to 99% as determined by isotopic dilution with highly purified nonlabeled carbamate. Radioautography of developed thin layer chromatograms—silica gel G plates with 3 to 1 ether–benzene—indicated several minor impurities between the origin and the spot corresponding to that of the desired carbamate at R_f 0.4 to 0.5. These impurities are artifacts owing to oxidation or hydrolysis of the carbamate on the gel surface and may be minimized by carrying out the chromatography under an inert atmosphere (*17*).

III $X^1 = X^3 = C$; $X^2 = C^{14}$

IV $X^2 = X^3 = C$; $X^1 = C^{14}$

V $X^1 = X^2 = C$; $X^3 = C^{14}$

Studies of plant (*4, 8*) and animal (*7*) metabolism of Temik have shown the corresponding Temik sulfoxide (VIII) to be a major metabolite. A labeled sample of this material was prepared by the oxidation of *N*-methyl-C^{14} Temik with one equivalent of peracetic acid. Under these conditions the sulfoxide, obtained in high yield, was contaminated with only minor quantities of the corresponding sulfone.



VIII

All syntheses described in this paper were preceded by a series of preliminary experiments employing nonradioactive materials to optimize yields and techniques. In each instance, the products were characterized either by physical data such as melting point, boiling point, or vapor pressure, or by infrared and NMR spectral analysis. The radiochemical purities of the final products were verified by radioautography and by isotopic dilution analysis.

Experimental

All liquid reagents used in the syntheses were fractionally distilled. The labeled carbon dioxide, acetic acid, acetyl chloride, *tert*-butyl alcohol, isobutylene, 2 - methyl - 2 - (methylthio)-propionaldehyde oxime, and 2-methyl-2 - (methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime were purified on a high vacuum manifold. All temperatures are uncorrected. Yields are based on the radiolabeled intermediate employed in each instance.

Sodium Acetate-1-C^{14} (*1*). Methyl magnesium bromide in diethyl ether (5.2 ml., 2.91 mmoles) was carbonated with carbon dioxide-C^{14} (2.02 mmoles, 40.0 mc.) by stirring for 2 hours at room temperature. The complex formed was hydrolyzed with 6.0 ml. of water followed by an excess of 10% aqueous sulfuric acid. The resulting acetic-1-C^{14} acid was extracted continuously with ether into a flask containing a slight excess of sodium hydroxide solution. The aqueous layer of this solution was evaporated on a steam bath under a stream of nitrogen and the sodium acetate dried under vacuum at 120° C. The yield of sodium acetate-1-C^{14} (169.1 mg., 2.06 mmoles) was quantitative.

Acetic-1-C^{14} Acid (*5*). Labeled sodium acetate (169.1 mg., 2.06 mmoles was transferred to a porcelain boat which was placed in a borosilicate glass combustion tube—1.8 × 65 cm.—enclosed in an

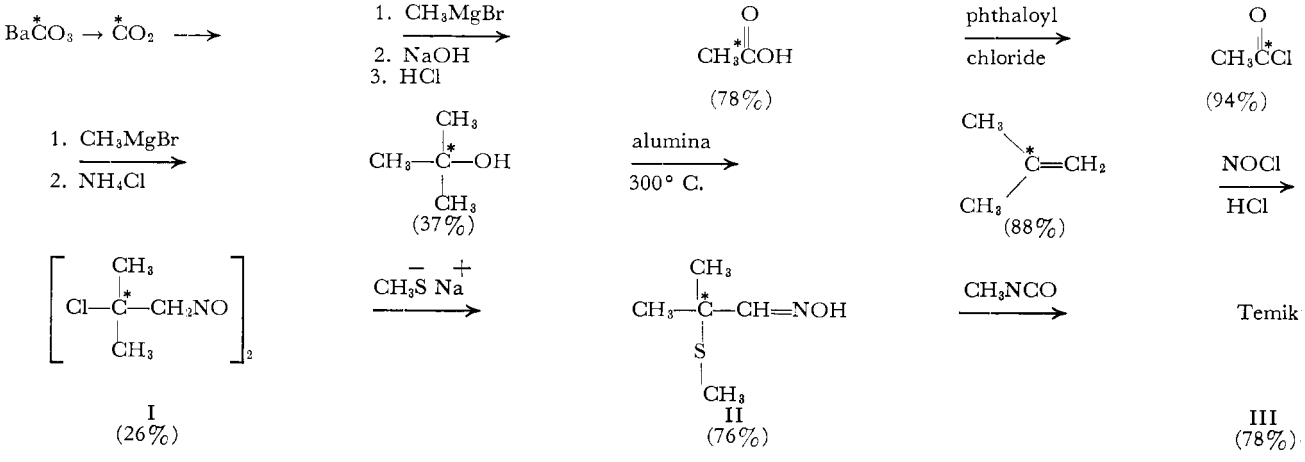


Figure 1. Synthesis of Temik

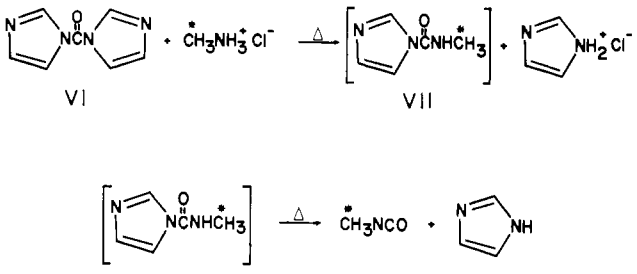


Figure 2. Synthesis of *N*-methyl-C^{14} Temik

open end furnace. The assembly was attached via dry ice traps to a vacuum manifold, and dry hydrogen chloride was passed through the tube for 2.5 hours while the internal temperature was raised to 120° C. After sweeping the tube with helium for 0.5 hour to facilitate the removal of hydrogen chloride, the entire system was evacuated to 0.1 micron pressure, and the traps containing the acetic acid were isolated from the combustion tube. Residual hydrogen chloride was removed by periodically warming the dry ice traps to room temperature and immediately recooling to −78° C. The yield of acetic-1-C^{14} acid was 97.0 mg. or 78%.

Acetyl-1-C^{14} Chloride (*5*). Acetic-1-C^{14} acid (97.0 mg., 1.61 mmoles) was diluted with nonlabeled acetic acid (384.3 mg., 6.4 mmoles, A.R. grade) and distilled in vacuo into a small reaction flask. Then dry air was admitted to the apparatus while phthaloyl chloride (5.8 ml., 400% excess, A.R. grade) was introduced quickly. The acetic acid was allowed to melt and the reactants were mixed by gentle shaking. The reaction mixture was then heated to 120° C. over a 45-minute period, and the evolved acetyl chloride was swept with dry nitrogen into a dry ice–cooled trap. Purification of the acetyl chloride was effected by alternately warming and cooling the product to remove entrained hydrogen chloride. The yield of acetyl-1-C^{14} chloride (589.6 mg., 7.51 mmoles) was 94%.

2-Methyl-2-propanol-2-C^{14}. A modified Roberts, McMahon, and Hine method (*15*) was used. Acetyl-1-C^{14} chloride (589.6 mg., 7.51 mmoles) was distilled in vacuo into a 15-ml. flask containing a side arm sealed with a serum cap. Methyl magnesium bromide in diethyl ether (10.78 ml., 17.25 mmoles) was added then to the chilled (liquid nitrogen) acetyl chloride from a hypodermic syringe. The solution was warmed to −5° C., maintained at this temperature for 2 hours with vigorous magnetic stirring, and allowed to stand overnight at room temperature. Excess saturated ammonium chloride solution was added to decompose the Grignard complex, and the solution was stirred magnetically and extracted continuously with ether for 24 hours. The ether solution was dried over anhydrous calcium sulfate after which the tertiary alcohol was isolated by vacuum distillation. The yield of 2-methyl-2-propanol-2-C^{14} (207.5 mg., 2.8 mmoles) was 37%.

Isobutylene-2-C^{14}. A modified Black, Wright, and Coull method (*3*) was used in the vapor phase dehydration of 2 - methyl - 2 - propanol - 2 - C^{14}. The labeled tertiary alcohol (207.5 mg., 2.8 mmoles) was distilled in vacuo into a small receiver and attached to a Vycor dehydration tube—containing 34 grams of activated F 110 Alcoa Alumina—enclosed in a Fisher micro combustion furnace. The furnace was heated to 300° C. and kept at this temperature for 4.5 hours while a stream of helium gas swept the labeled tertiary alcohol vapors through the hot alumina packing. The evolved isobutylene was collected in a series of traps immersed in dry ice and liquid nitrogen. Purification was effected by a cold trap distillation on the vacuum manifold giving an 88% yield (2.45 mmoles) of isobutylene-2-C^{14}.

2 - Chloro - 2 - methyl - 2 - C^{14} - 1-nitrosopropane Dimer. A modified procedure of Yakubovich and Lemke (*10, 19*) was employed. Isobutylene-2-C^{14} (2.45 mmoles) was distilled in vacuo into a small reaction flask containing a mixture of 844 mg. of concentrated hydrochloric acid and 991 mg. of freshly distilled isopropyl alcohol. The reaction flask was connected via a side arm equipped with a stopcock to a second vessel containing 207 mg. (3.16 mmoles) of redistilled nitrosyl chloride. By maintaining the isobutylene reaction mixture at −30° C. and the nitrosyl chloride at −5° C., a vapor pressure differential of several hundred millimeters was created between the two vessels. Through careful manipulation of the stopcock, the nitrosyl chloride was allowed to vaporize into the reaction flask over a period of 1.5 hours. The resulting white precipitate was diluted with 15 ml. of water, stirred well, and then filtered by suction. The solid was washed with 10 ml. of water and allowed to dry for 24 hours under vacuum. The yield was 76.9 mg. (26%) of white crystalline dimer, m.p. 95–98° C.

2 - Methyl - 2 - (methylthio)propionaldehyde-2-C^{14} Oxime (*11–13*). A solution of 2 - chloro - 2 - methyl-2 - C^{14} - 1 - nitrosopropane dimer (75.9 mg., 0.312 mmoles) in 0.5 ml. of absolute ethanol was prepared and was added immediately to an ethanol solution of sodium ethoxide (0.46 ml., 0.624 mmoles) and methyl mercaptan (38.5 mg., 0.80 mmoles) in a small reaction flask. The flask was fitted with a reflux condenser and was stirred at 40° C. while protected from the atmosphere with an Ascarite tube. After 1 hour, the vessel was attached to a vacuum manifold and the ethanol distilled into a chilled trap at 80 mm. pressure. The reaction flask then was warmed to 60° C. and the oxime distilled at 0.1 micron pressure into a trap chilled in liquid nitrogen. When distillation had ceased, the product was rinsed from the trap and tubing with 1 ml. of diethyl ether. Evaporation of the solvent gave 63.5 mg. (76%) of colorless oxime.

2 - Methyl - 2 - (methylthio)propionaldehyde - 2 - C^{14} *O* - (Methylcarbamoyl)oxime. 2 - Methyl - 2-(methylthio)propionaldehyde - 2 - C^{14} oxime (53.1 mg., 0.398 mmoles) was transferred into a 16-mm. diameter heavy-walled borosilicate glass tube 15 cm. long, with an 8-mm. diameter constriction near one end to facilitate sealing. A solution containing 0.20 ml. of xylene (A.R. grade) and 0.1 ml. of triethylamine (A.R. grade) catalyst was added to the reaction tube, 0.429 mmoles of methyl isocyanate was distilled into the constricted tube, and the tube was flame-sealed. The mixture was warmed to room temperature and agitated for 18 hours. The tube was cooled to −25° C., opened, and the supernatant liquid was removed by filtration through a fine grade fritted-glass filter stick attached to a suction flask. The solid methylcarbamoyloxime was washed with a minimum amount of cold xylene. Any residual solvent was removed by evacuating for 3 hours at 80 mm. pressure. A total of 59.1 mg. (78% yield) of radioactive product containing 1.22 mc. of carbon-14 was obtained. The product had a melting point (98.5−100° C.) identical to pure Temik and a radiochemical purity of 99% as determined by isotope dilution. The over-all yield of Temik from carbon dioxide was 4%.

2 - Methyl - 2 - (methyl - C^{14} - thio)-propionaldehyde *O* - (Methylcarbamoyl)oxime. The precursor 2-methyl-2 - (methyl - C^{14} - thio)propionaldehyde oxime was prepared by treating 2-chloro-2 - methyl - 1 - nitrosopropane dimer (140.9 mg., 0.58 mmoles) with 5 mc. (1.26 mmoles) of methyl-C^{14}-mercaptan (New England Nuclear Corp., Boston, Mass.) as previously described. A solution of the oxime (0.96 mmoles) and a trace of triethylamine in xylene was treated with 1.09 mmoles of methyl

isocyanate as described above to give the carbamate in 64% over-all yield. The labeled product (154 mg., 0.812 mmoles, 4.0 mc.), m.p. 98.5–100° C., had a radiochemical purity of 98.5% by isotopic dilution analysis.

Methyl-C^{14} Isocyanate. The following procedure is representative of a typical methyl-C^{14} isocyanate synthesis.

A mixture of 90.7 mg. (0.56 mmole) of *N*, *N'*-carbonyldiimidazole (*9*), 16.2 mg. of methyl-C^{14}-amine hydrochloride (*6*) (1.73 mc.), and 13.5 mg. (0.44 mmole total) of nonlabeled methylamine hydrochloride was introduced into a 9 × 155 mm. pyrolysis tube. After the reactants were mixed, the tube was connected to a vacuum manifold and the system evacuated to 13 mm. The system was isolated from the pump by means of a stopcock and the reaction mixture was warmed carefully. As the materials melted, a vigorous evolution of methyl isocyanate was observed. Heating was continued at such a rate as to maintain a smooth boiling action and reflux in the lower portion of the pyrolysis tube. Care was taken to avoid spattering of the reaction mixture over the walls of the tube and into the manifold. The pressure within the system rose to a maximum of 22 mm. during the pyrolysis even though a liquid nitrogen–cooled trap was incorporated in the system to condense the liberated isocyanate. Heating was continued for a total of 1 hour. During the latter 30 minutes of this period, the pressure slowly dropped to the original 13 mm. After the reaction mixture was cooled the system was further evacuated to 0.2 mm. and the contents were reheated as before. Preliminary experiments with nonlabeled materials consistently gave 20 to 25% higher yields of isocyanate when this last step was carried out. After about 15 minutes at this pressure, heating was no longer effective owing to distillation and sublimation of the reaction mixture over the walls of the reaction tube. The yield of methyl-C^{14} isocyanate was about 75% as determined manometrically in a calibrated system. Yields with nonlabeled methylamine hydrochloride were consistently 80 to 85%.

2 - Methyl - 2 - (methylthio)propionaldehyde *O* - (Methyl - C^{14} - carbamoyl)oxime. A mixture of 23.1 mg. (0.174 mmole) of 2-methyl-2-(methylthio)propionaldehyde oxime, 150 μl. of dry *n*-hexane, one microdrop of triethylamine and several seed crystals of Temik in a 1 × 5 cm. tube were frozen in liquid nitrogen. With the aid of a vacuum manifold, 4.5 mg. (0.08 mmole) of freshly prepared methyl-C^{14} isocyanate (0.57 mc.) was allowed to distill into the tube containing the oxime solution. The reaction mixture was sealed by means of a stopcock and allowed to stand overnight at room temperature. The following morning the crystalline mass was cooled in an ice bath and the mother liquor carefully removed with a syringe. After being washed with two 100-μl. portions of *n*-hexane and drying, the product was recrystallized from 70 μl. of hot isopropyl ether and dried in vacuo to give 11.9 mg. (0.446 mc., 78%) of 2 - methyl-2 - (methylthio)propionaldehyde *O*-(methyl-C^{14}-carbamoyl)oxime.

2 - Methyl - 2 - (methylsulfinyl)-propionaldehyde *O*-(Methyl-C^{14}-carbamoyl)oxime. A solution of 334.9 mg. (1.76 mmoles) of 2 - methyl - 2 - (methylthio)propionaldehyde *O* - (methyl - C^{14} - carbamoyl)oxime (27 μc.) in 3.5 ml. of ethyl acetate was cooled in an ice bath. To this solution, 657.7 mg. (1.77 mmole) of 20.5% peracetic acid in ethyl acetate (*14*) was added dropwise with occasional swirling and continued cooling over a 45-minute period. The partially crystalline reaction mixture was treated with 20 ml. of cold *n*-pentane added in small portions over 2 hours. When crystallization had ceased, the mixture was cooled briefly in a dry ice–acetone bath and the mother liquor removed with a syringe. The crystalline residue was washed with two 20-ml. portions of cold 1 to 5 ethyl acetate–pentane, filtered, and dried in vacuo to give 315 mg. (87%) of the desired sulfoxide, m.p. 106–107° C. The product can be stored for long periods at −10° C. but deteriorates after several weeks at room temperature, as evidenced by its turning yellow and liquefying.

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