toxicity to mice suggest the possibility of a related oxabicycloheptane target site in plants and mammals.

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Pyrolysis of Triallate

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The thermal chemistry of triallate [*S*-(2,3,3-trichloro-2-propenyl) diisopropylthiocarbamate, **1**] was examined to determine whether the thermal chemistry of thiocarbamate *S*-ester herbicides can be predicted from thermal reactions of simpler carbamates. Flash vacuum pyrolysis of **1** at 475–575 °C yields a complex mixture of products. Products were identified by gas chromatography–mass spectrometry analysis of the pyrolysate. 1,1,2-Trichloro-1-butene (**7**) was the major product. Minor products included 1,1,2,5,6,6-hexachloro-1,5-hexadiene (**21**), 1,1-dichloro-1,2-butadiene (**5**), and 4,5-dihydro-3-isopropyl-4-methylthioazolidin-2(3*H*)-one (**18**). The major reaction mechanism involves formation and reactions of 1,1,2-trichloroallyl and diisopropylthiocarbamoyl radicals. Thermal reactions of structurally analogous carbamates can be used to predict the thermal chemistry of other thiocarbamate *S*-ester herbicides.

Previous studies of herbicide thermal chemistry have focused on the bulk stability of the herbicide and largely ignored the thermal decomposition products (Saito et al., 1981; Stojanovic et al., 1972). Herbicide thermal reaction products and reaction mechanisms could be predicted if the thermal chemistry of suitable analogues was well established. The thermal chemistry of thiocarbamate *S*-ester

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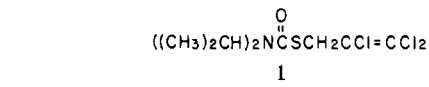
herbicides should resemble the thermal chemistry of simpler carbamates, thiocarbamate *O*-esters, and dithiocarbamates. Unfortunately, the structural features in thiocarbamate *S*-esters responsible for effective herbicidal activity are quite different from the structural features of the model carbamates (Daly and Ziolkowski, 1971), thiocarbamate *O*-esters (Newman and Hetzel, 1969), and dithiocarbamates (Moharir, 1975; Chande, 1979) used to determine the thermal chemistry of these functional groups. We have examined the thermal chemistry of a representative thiocarbamate *S*-ester herbicide, triallate [1; *S*-(2,3,3-trichloro-2-propenyl) diisopropylthiocarbamate], to determine how the structural features of triallate affect the thermal chemistry of the thiocarbamate *S*-ester functional group.



1

EXPERIMENTAL SECTION

Chemicals. Solvents were reagent grade and were used as received. Triallate and 1,1,2,3-tetrachloropropene were received as gifts from Monsanto (St. Louis, MO). Triallate was recrystallized from hexane until pure by GC (mp 28–30 °C), and 1,1,2,3-tetrachloropropene was distilled under vacuum [b.p. 22–24 °C (0.2 mm)]. *n*-Undecane (99%), isopropylamine (99%), 1,2,3,4-tetrachlorobenzene (98%), 1,2,3,5-tetrachlorobenzene (99%), and 1,2,4,5-tetrachlorobenzene (98%) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Silica gel (Baker Analyzed Reagent, 60–200 mesh) obtained from J. T. Baker Chemical Co. (Phillipsburg, NJ) was used as received.

Synthesis of 4-Methyl-1,1,2-trichloro-1-pentene (14) and 4-Methyl-2,3,3-trichloro-1-pentene (16). A solution of isopropylmagnesium bromide in ether (50 mL) was prepared from isopropyl bromide (4.86 mL, 51.4 mmol) and Mg (1.25 g, 51.4 mmol). 1,1,2,3-Tetrachloropropene (3.0 mL, 26 mmol) in ether (25 mL) was added dropwise to the stirred solution over a 30-min period. After an additional 30 min, the reaction was quenched by pouring on 2 M H_2SO_4 (50 mL) and ice (200 g). The ether layer was separated and the aqueous phase extracted with ether (2 × 50 mL). The ether layers were dried over $MgSO_4$. The solution was filtered and the ether evaporated to yield a liquid (3.9 g) that contained **8** (28%), **14** (43%), **16** (29%), and numerous minor components. The mixture was distilled [70–90 °C (15 mm)] to yield a fraction enriched in **14** and **16**. Repeated chromatography on neutral alumina (pentane) gave a fraction containing **14** and **16** (0.44 g) and a fraction containing nearly pure **16** (0.08 g). The mass spectra of these compounds were identical with the mass spectra of **14** and **16** obtained from analysis of a triallate pyrolysate.

Isolation of 4,5-Dihydro-3-isopropyl-4-methylthiazolidin-2(3*H*)-one (18). Triallate (2.0 g, 6.7 mmol) was pyrolyzed [575 °C (0.2 mm)] to yield a dark red oil (1.7 g). The oil was subjected to chromatography on silica gel (8 g, 60–200 mesh) using pentane as the eluent. Fractions were monitored by gas chromatography as the elutent was gradually changed to methylene chloride. Compound **18**, contaminated with triallate and other compounds, came off the column as the eluent was changed to methanol. This mixture (0.154 g) was subjected to chromatography on silica gel (6 g) using 1% methylene chloride in pentane to remove the triallate. Elution with methanol gave an impure sample of **18**. This mixture (0.08 g) was subjected to chromatography on silica gel (3 g) using 5% acetone in methylene chloride. Compound **18** (0.05 g) was isolated in about 95% purity. IR ($CHCl_3$): 3013, 2977, 2939, 1658, 1401, 1370, 1236, 1202 cm^{-1}. ^1H NMR ($Me_4Si/CDCl_3$): δ 1.0–1.6 (m, 9 H), 2.82 (dd, J = 3.0, 10.8 Hz, 1 H), 3.50 (dd, J = 7.6, 10.8 Hz, 1 H), 3.87–4.27 (m, J(apparent) = 6.9, 7.6 Hz, 2 H). ^{13}C NMR ($Me_4Si/CDCl_3$): δ 20.38 (q), 20.57 (q), 21.38 (q), 34.32 (t), 47.10 (d), 53.83 (d), 170.55 (s).

Synthesis of 1,1,2,5,6,6-Hexachloro-1,5-hexadiene (21). Anhydrous pyridine (200 mL) and powdered copper (5.0 g, 79 mmol) were combined in a 500-mL round-bottom flask and sonicated under nitrogen with a Branson B-220 ultrasonic cleaner for 1 h. 1,1,2,3-Tetrachloro-1-propene (3.0 mL, 26 mmol) was syringed into the slurry. The mixture was sonicated for an additional 4 h. The slurry was centrifuged, and the solution was decanted from the solids. The solution was diluted with pentane (100 mL), extracted with 10% HCl (2 × 100 mL), and dried over $MgSO_4$. The solution was filtered and evaporated to yield a liquid (50 mg) that was approximately 90% one component by gas chromatographic analysis. The mass spectrum of the major component was identical with the mass spectrum of **21** prepared by pyrolysis of triallate.

Pyrolysis Apparatus. The apparatus consisted of a horizontally mounted, unpacked quartz tube (2.2-cm i.d.) heated by a Lindberg heavy-duty laboratory furnace (Model 59814) to give a hot zone of 45 cm. The pyrolysis tube was connected to a cold trap that was connected to a vacuum manifold. A sample reservoir was connected to the other end of the pyrolysis tube. All connections were made with ground-glass joints. Pressures were measured at the manifold. Portions of the pyrolysis tube projecting from the furnace were wrapped with heating tape.

Vacuum Pyrolysis of Triallate. The furnace and pyrolysis tube were brought to the desired temperature. Triallate (100 mg, 0.33 mmol) was loaded into the sample reservoir, and the apparatus was assembled. The sample reservoir was cooled in liquid nitrogen, and the apparatus was evacuated (0.2 mm). The sample reservoir was allowed to warm for 5 min before the trap was cooled with liquid nitrogen. The sample reservoir was warmed with a heat gun to force the triallate through the pyrolysis tube. About 90 s was necessary to complete the vaporization. The vacuum was maintained for another 10 min. Then the vacuum was broken, and the trap was removed from the apparatus and fitted with a septum and a $CaCl_2$ drying tube. The tube was allowed to warm to room temperature, and the pyrolysate was taken up in methanol. *n*-Undecane (2.5 mg, 0.016 mmol) was added, and the sample was analyzed by gas chromatography or gas chromatography–mass spectrometry. No attempt was made to trap and analyze any gaseous products. This procedure was followed for pyrolyses at 475, 500, 525, 550, and 575 °C.

Analytical Procedures. ^1H NMR spectra were recorded on a Varian Associates EM-390 90-MHz nuclear magnetic resonance spectrometer. ^{13}C NMR spectra were recorded on a JEOL FX-90Q 90-MHz nuclear magnetic resonance spectrometer. Carbon multiplicities were determined by the method of LeCocq and Lallemand (1981). IR spectra were recorded on a Mattson Instruments Cygnus 25 FT-IR spectrometer.

Gas chromatographic analyses were performed with a Varian Associates 3700 gas chromatograph (flame ionization detector) equipped with a DB-1 capillary column (30 m × 0.33 mm (i.d.), J & W Scientific). The carrier gas (He) flow was 1 mL/min. A temperature program (40 °C/5 min, 10 °C/min, 230 °C/10 min) was used for all analyses. The gas chromatograph was interfaced to a Shimadzu

Chromatopac C-R3A integrator. All compounds, except triallate, were quantified by comparison to an internal standard without consideration for response factors. The triallate response factor was determined. Isopropylamine was identified by retention time and co-injection studies.

Gas chromatography–mass spectrometry (GC–MS) was performed on a Hewlett-Packard Model 5992-A gas chromatograph–mass spectrometer equipped with a Hewlett-Packard ultraperformance, cross-linked methylsilicone fused silica capillary column (25 m × 0.31 mm (i.d.)). The carrier gas (Ar) flow rate was 1 mL/min. All analyses were cool, on-column injections with a temperature program (40 °C/5 min, 10 °C/min, 300 °C/10 min). Ionization was by electron impact (70 eV). The mass range scanned was 40–500 amu. Total ion abundances for each mass spectrum were usually greater than 1000 ions. Sufficient quantities of minor products for GC–MS analysis were obtained from high-temperature pyrolysates. The combination of several pyrolysates and concentration by column chromatography was necessary for some very minor products. Product identifications were verified by GC–MS analysis of commercial samples of **1**, **13**, **17a**, **17b**, and **19** and synthetic samples of **11**, **14**, **16**, and **21**. The mass spectra of **2** and **4** were the same as mass spectra found in the literature. Compounds **6**–**11**, **15**, and **21** are known compounds, but their mass spectra have not been reported. Compounds **5**, **12**, **14**, **16**, **18**, and **22** are new compounds.

Carbon oxysulfide (2): m/z (relative abundance) 62 (6.1), 61 (2.4), 60 (100).

1,1-Dichloro-1,2-propadiene (4): m/z (relative abundance) 112 (2.8), 111 (1.1), 110 (15.8), 109 (4.4), 108 (23.3), 107 (4.8), 84 (2.9) 82 (4.7), 76 (1.7), 75 (31.7), 74 (9.0), 73 (100), 72 (17.1), 71 (5.9), 67 (1.5), 61 (1.3), 60 (1.0), 59 (1.8), 56 (1.3), 49 (4.7), 47 (14.4), 45 (1.9), 44 (19.4), 43 (4.5), 42 (3.1), 41 (2.8).

1,1-Dichloro-1,2-butadiene (5): m/z (relative abundance) 126 (5.0), 125 (1.5), 124 (31.0), 122 (46.0), 110 (1.1), 109 (1.6), 108 (1.8), 107 (1.4), 104 (1.0), 102 (2.4), 98 (2.0), 96 (2.7), 90 (2.2), 89 (26.3), 88 (12.8), 87 (88.9), 86 (21.9), 85 (5.3), 84 (2.1), 83 (1.4), 75 (1.3), 74 (1.2), 71 (1.1), 65 (2.1), 64 (1.7), 63 (7.0), 62 (4.9), 61 (17.3), 60 (6.2), 59 (2.2), 53 (4.9), 52 (16.8), 51 (100), 50 (56.0), 49 (19.6), 48 (4.1), 47 (3.9), 45 (1.2), 44 (11.9), 43 (3.5), 42 (1.1), 41 (4.8).

2,3,3-Trichloropropene (6): m/z (relative abundance) 146 (3.9), 144 (3.9), 120 (4.3), 118 (4.3), 113 (5.7), 112 (4.3), 111 (48.3), 109 (50.0), 97 (7.8), 94 (8.3), 85 (10.9), 83 (19.6), 82 (5.7), 81 (12.2), 80 (7.0), 79 (13.0), 77 (5.2), 75 (9.1), 74 (6.1), 73 (13.9), 70 (5.7), 69 (11.7), 68 (40.4), 63 (5.7), 61 (9.1), 60 (5.7), 57 (5.2), 56 (7.4), 55 (53.5), 54 (13.0), 53 (13.0), 52 (7.4), 51 (8.3), 50 (1.7), 49 (7.4), 47 (6.1), 45 (2.6), 43 (41.3), 42 (37.4), 41 (41.3).

1,1,2-Trichloro-1-butene (7): m/z (relative abundance) 164 (1.9), 163 (1.4), 162 (3.3), 160 (28.5), 158 (32.5), 156 (1.4), 147 (8.9), 146 (1.2), 145 (32.2), 144 (0.9), 143 (32.0), 140 (2.6), 138 (3.3), 137 (2.8), 132 (3.0), 131 (2.6), 130 (6.1), 129 (2.8), 127 (3.7), 126 (5.4), 125 (45.3), 123 (87.4), 122 (3.3), 121 (4.7), 120 (6.3), 119 (4.0), 118 (5.1), 117 (3.7), 108 (2.6), 107 (10.3), 105 (5.4), 100 (3.3), 97 (3.5), 95 (6.3), 94 (10.0), 89 (35.5), 88 (6.3), 87 (96.0), 86 (6.8), 85 (53.0), 84 (14.3), 83 (28.0), 82 (13.8), 81 (8.2), 75 (14.0), 74 (4.7), 73 (43.5), 72 (14.7), 71 (4.0), 70 (7.0), 69 (3.5), 68 (6.5), 65 (4.0), 63 (18.0), 62 (16.4), 61 (32.0), 60 (11.7), 59 (11.4), 57 (3.0), 54 (4.0), 53 (24.3), 52 (15.9), 51 (100), 50 (72.7), 49 (38.8), 48 (12.6), 47 (32.2), 44 (8.2), 43 (3.7), 41 (5.6).

2,3,3-Trichloro-1-butene (8): m/z (relative abundance) 158 (5.9), 140 (15.7), 138 (31.4), 125 (9.8), 123 (23.5), 105 (39.2), 103 (86.3), 102 (5.9), 96 (19.6), 89 (37.3), 87 (54.9), 85 (21.6), 83 (19.6), 75 (49.0), 73 (29.4), 67 (100), 65 (64.7), 63 (29.4), 62 (21.6), 61 (39.2), 59 (7.8), 53 (25.5), 52 (19.6), 51 (49.0), 50 (11.8), 42 (3.9), 41 (47.1).

1,1,4-Trichloro-1,2-butadiene (9): m/z (relative abundance) 160 (6.7), 158 (18.3), 156 (21.7), 125 (6.7), 123 (50.0), 121 (100), 109 (21.7), 107 (28.3), 96 (36.7), 94 (16.7), 87 (3.3), 86 (21.7), 85 (70.0), 84 (23.0), 61 (20.0), 60 (16.7), 51 (48.3), 50 (45.0), 49 (41.7), 47 (23.3), 45 (16.7), 44 (18.3), 42 (1.7).

2,3,3,3-Tetrachloropropene (10): m/z (relative abundance) 180 (3.1), 178 (4.6), 147 (26.2), 146 (6.2), 145 (98.5), 143 (100), 123 (1.5), 121 (16.9), 119 (20.0), 117 (18.5), 111 (12.3), 109 (20.0), 107 (18.5), 102 (20.0), 87 (4.6), 85 (43.1), 84 (20.0), 83 (80.0), 82 (21.5), 75 (29.2), 74 (21.5), 73 (56.9), 72 (46.2), 63 (18.5), 61 (41.5), 59 (18.5), 49 (29.2), 47 (40.0), 45 (13.8), 42 (4.6).

***N*,*N*-Diisopropylformamide (11)**: m/z (relative abundance) 129 (3.9), 128 (35.9), 123 (2.4), 112 (6.0), 100 (3.1), 98 (8.1), 96 (5.5), 87 (3.7), 86 (25.7), 85 (23.2), 84 (6.8), 73 (3.9), 71 (4.5), 70 (50.3), 69 (8.6), 68 (8.4), 65 (3.1), 60 (5.2), 59 (100), 57 (2.9), 56 (6.3), 55 (5.8), 54 (8.6), 51 (2.6), 45 (4.5), 44 (28.3), 43 (61.3), 42 (24.3), 41 (30.6).

3,4,4-Trichloro-3-butenal (12): m/z (relative abundance) 176 (6.8), 174 (18.2), 172 (18.2), 147 (22.7), 146 (11.4), 145 (75.0), 144 (11.4), 143 (65.9), 139 (18.2), 137 (31.8), 134 (20.5), 132 (50.0), 130 (59.1), 123 (27.3), 111 (50.0), 110 (36.4), 109 (68.2), 108 (43.2), 107 (22.7), 103 (22.7), 101 (59.1), 87 (13.6), 85 (61.4), 84 (20.5), 83 (61.4), 75 (50.0), 73 (100), 72 (25), 65 (79.5), 63 (34.1), 62 (22.7), 61 (36.4), 59 (34.1), 53 (27.3), 51 (52.3), 50 (34.1), 49 (34.1), 47 (27.3), 45 (20.5), 44 (93.2), 42 (29.0), 41 (38.6).

1,1,2,3-Tetrachloropropene (13): m/z (relative abundance) 184 (1.6), 182 (7.7), 180 (15.1), 178 (11.9), 149 (3.6), 148 (1.5), 147 (31.0), 146 (4.0), 145 (99.0), 143 (100), 141 (1.0), 131 (1.3), 129 (1.7), 119 (2.6), 117 (2.7), 111 (2.8), 110 (1.6), 109 (12.7), 108 (4.3), 107 (21.8), 106 (1.8), 103 (1.0), 98 (1.2), 96 (2.0), 94 (2.8), 87 (5.0), 86 (1.3), 85 (30.5), 84 (6.3), 83 (46.6), 82 (8.8), 75 (8.9), 74 (7.4), 73 (29.2), 72 (19.0), 71 (8.8), 68 (1.6), 67 (2.5), 63 (1.3), 62 (1.0), 61 (6.6), 60 (3.3), 54 (2.2), 53 (5.0), 51 (3.4), 50 (1.2), 49 (18.5), 48 (3.4), 47 (24.5).

1,1,2-Trichloro-4-methyl-1-pentene (14): m/z (relative abundance) 191 (0.1), 190 (1.1), 189 (0.2), 188 (2.2), 187 (0.3), 186 (2.5), 185 (0.1), 149 (0.4), 148 (1.1), 147 (1.0), 146 (3.0), 145 (2.8), 144 (3.6), 143 (2.5), 111 (1.3), 110 (0.7), 109 (3.1), 108 (0.6), 107 (1.3), 99 (2.5), 87 (1.5), 85 (3.8), 84 (1.1), 83 (5.8), 77 (1.6), 75 (3.3), 74 (1.2), 73 (10.7), 72 (2.7), 65 (1.0), 63 (2.6), 62 (1.5), 61 (1.4), 53 (1.3), 51 (3.5), 50 (2.0), 49 (3.4), 47 (2.4), 44 (3.2), 43 (100), 42 (27.1).

***O*-Methyl diisopropylcarbamate (15)**: m/z (relative abundance) 160 (1.8), 159 (13.2), 145 (4.8), 144 (57.2), 143 (1.1), 129 (1.2), 128 (3.7), 116 (4.7), 103 (5.4), 102 (100), 101 (1.5), 86 (8.2), 84 (7.0), 73 (3.3), 72 (6.9), 71 (1.0), 70 (13.7), 68 (1.2), 59 (19.1), 58 (40.1), 57 (3.3), 56 (9.5), 55 (1.0), 54 (1.4), 45 (1.1), 44 (11.2), 43 (29.8), 42 (20.9), 41 (23.1), 40 (3.2).

2,3,3-Trichloro-4-methyl-1-pentene (16): m/z (relative abundance) 188 (3.4), 186 (4.5), 155 (3.4), 154 (6.8), 153 (15.9), 151 (23.9), 137 (8.0), 125 (10.2), 123 (13.6), 115 (23.9), 111 (15.9), 109 (13.6), 101 (19.3), 100 (14.8), 99 (35.2), 96 (13.6), 89 (15.9), 87 (22.7), 85 (19.3), 83 (14.8), 81 (12.5), 80 (14.8), 79 (75.0), 77 (59.1), 75 (27.3), 73 (22.9), 72 (17.0), 70 (6.8), 65 (37.5), 63 (23.9), 62 (12.5), 61 (12.5), 59 (100), 58 (10.2), 57 (22.7), 56 (13.6), 55 (22.7), 53 (26.1), 52 (10.2), 51 (21.6), 50 (14.8), 49 (15.9), 45 (6.8), 44 (11.4), 42 (13.6), 41 (47.7).

4,5-Dihydro-3-isopropyl-4-methylthiazolidin-2-(3*H*)-one (18): *m/z* (relative abundance) 161 (3.1), 160 (6.6), 159 (55.9), 158 (1.3), 146 (4.8), 145 (8.0), 144 (100), 143 (2.2), 130 (1.9), 118 (4.4), 117 (10.4), 116 (67.0), 115 (1.2), 104 (2.9), 103 (3.3), 102 (56.9), 101 (1.7), 89 (2.0), 88 (4.2), 85 (1.6), 84 (17.5), 83 (1.0), 76 (2.1), 75 (4.6), 74 (46.3), 73 (31.5), 72 (2.1), 71 (3.8), 70 (28.8), 69 (3.4), 68 (4.4), 67 (1.0), 61 (2.9), 60 (4.1), 59 (7.9), 58 (4.0), 57 (3.8), 56 (11.4), 55 (4.4), 54 (5.0), 52 (1.4), 48 (1.5), 47 (8.3), 46 (15.0), 45 (17.9), 44 (13.6), 43 (37.2), 42 (47.9), 41 (78.2), 40 (8.8).

1,1,2,4,4,5-Hexachloro-1,5-hexadiene (20): *m/z* (relative abundance) 292 (0.7), 290 (2.4), 288 (2.9), 286 (1.4), 253 (1.2), 221 (1.9), 219 (6.7), 218 (1.3), 217 (16.7), 215 (11.0), 203 (1.1), 186 (1.0), 185 (1.1), 184 (3.4), 183 (4.5), 182 (13.4), 181 (6.4), 180 (16.3), 179 (3.1), 171 (2.9), 170 (1.1), 169 (2.1), 168 (1.9), 167 (1.2), 166 (1.5), 164 (1.4), 158 (2.4), 157 (1.4), 156 (3.2), 155 (1.1), 154 (2.4), 149 (3.9), 148 (4.5), 147 (31.9), 146 (10.2), 145 (100), 143 (89.7), 136 (1.7), 135 (2.4), 134 (1.7), 133 (2.6), 132 (1.1), 131 (2.4), 129 (1.2), 124 (2.9), 123 (1.4), 122 (3.1), 121 (5.0), 120 (1.4), 119 (7.8), 117 (4.6), 113 (1.1), 112 (1.5), 111 (7.6), 110 (3.3), 109 (12.5), 108 (5.5), 107 (7.7), 106 (1.0), 98 (2.9), 97 (2.7) 96 (4.3), 95 (3.1), 94 (4.9), 92 (1.4), 91 (4.6), 90 (3.7), 89 (2.5), 88 (1.3), 87 (7.2), 86 (6.4), 85 (20.1), 84 (5.6), 83 (25.5), 82 (3.6), 77 (1.2), 76 (1.4), 75 (14.6), 74 (14.6), 73 (30.3), 72 (15.3), 71 (1.8), 70 (1.6), 65 (1.2), 64 (1.1), 63 (6.7), 62 (7.1), 61 (19.0), 60 (5.2), 59 (1.7), 56 (1.3), 55 (2.0), 51 (19.6), 50 (12.2), 49 (14.6), 48 (3.0), 47 (12.9), 43 (1.8), 42 (1.4).

1,1,2,5,6,6-Hexachloro-1,5-hexadiene (21): *m/z* (relative abundance) 290 (2.0), 288 (2.5), 286 (1.2), 257 (0.8), 255 (2.3), 253 (4.1), 251 (2.6), 219 (0.6), 217 (1.4), 183 (1.2), 182 (2.4), 181 (1.7), 180 (2.7), 179 (0.7), 149 (3.6), 148 (1.9), 147 (30.2), 146 (4.8), 145 (96.9), 143 (100), 123 (1.7), 122 (0.8), 121 (3.0), 120 (1.0), 119 (3.8), 117 (2.9), 111 (3.0), 110 (3.3), 109 (10.5), 108 (5.0), 107 (12.5), 99 (1.0), 98 (1.2), 97 (2.1), 96 (5.4), 95 (2.1), 94 (5.8), 91 (1.1), 90 (1.4), 87 (9.0), 86 (3.6), 85 (42.1), 84 (8.9), 83 (52.5), 82 (5.6), 75 (18.1), 74 (10.7), 73 (49.9), 72 (17.5), 71 (3.6), 63 (3.9), 62 (4.7), 61 (11.0), 60 (5.8), 59 (2.4), 55 (1.2), 51 (16.4), 50 (16.7), 49 (28.4), 47 (25.3).

2,3,3,4,4,5-Hexachloro-1,5-hexadiene (22): *m/z* (relative abundance) 294 (1.8), 292 (8.3), 291 (1.2), 290 (20.9), 289 (1.7), 288 (25.5), 286 (16.4), 255 (2.4), 253 (3.3), 251 (3.0), 239 (2.4), 237 (1.2), 221 (8.6), 220 (2.6), 219 (36.1), 218 (8.0), 217 (78.6), 216 (8.0), 215 (62.7), 206 (2.1), 205 (2.7), 204 (3.5), 203 (4.5), 202 (3.0), 201 (2.6), 194 (1.1), 190 (1.1), 186 (3.0), 185 (7.1), 184 (33.4), 183 (23.5), 182 (90.7), 181 (36.3), 180 (100), 179 (19.4), 177 (2.6), 172 (1.5), 171 (4.1), 170 (7.1), 169 (9.2), 168 (10.7), 167 (8.0), 166 (6.3), 164 (4.4), 163 (1.7), 162 (1.7), 161 (1.2), 160 (8.0), 159 (3.5), 158 (29.7), 157 (6.0), 156 (26.1), 155 (2.9), 154 (1.2), 151 (1.1), 150 (2.3), 149 (5.0), 148 (11.4), 147 (22.6), 146 (23.2), 145 (48.6), 143 (30.4), 141 (2.3), 137 (1.7), 136 (2.7), 135 (7.5), 134 (6.9), 133 (16.1), 132 (2.1), 131 (5.4), 130 (3.6), 129 (3.3), 127 (2.6), 126 (3.8), 125 (2.7), 124 (9.9), 123 (9.3), 122 (20.3), 121 (22.3), 120 (4.2), 119 (28.0), 117 (18.8), 113 (3.5), 112 (3.0), 111 (24.2), 110 (14.3), 109 (44.4), 108 (16.1), 107 (28.9), 105 (2.3), 103 (1.2), 99 (3.6), 98 (5.1), 97 (11.1), 96 (15.2), 95 (6.0), 94 (18.1), 92 (5.1), 91 (13.7), 90 (13.4), 89 (8.4), 88 (3.9), 87 (23.9), 86 (11.1), 85 (92.5), 84 (28.3), 83 (71.4), 82 (10.4), 77 (4.8), 76 (3.0), 75 (40.2), 74 (50.9), 73 (88.7), 72 (38.7), 70 (2.1), 65 (1.2), 64 (1.2), 63 (22.7), 62 (20.0), 61 (51.7), 60 (17.2), 59 (5.6), 56 (3.0), 55 (9.2), 54 (8.3), 53 (2.4), 52 (9.3), 51 (68.2), 50 (63.0), 49 (56.6), 48 (12.2), 47 (37.8), 44 (3.3), 42 (1.7).

RESULTS AND DISCUSSION

Pyrolysis of Triallate. Triallate (1) undergoes extensive decomposition when subjected to flash vacuum pyrolysis at temperatures greater than 500 °C (Table I). Gas chromatographic analysis of the pyrolysate showed that five major and numerous minor nongaseous products are formed at 525 °C (Figure 1). Higher temperatures resulted in more extensive triallate decomposition and an increase in the number and quantity of minor products (Table I). No evidence was obtained for products with molecular weights greater than the molecular weight of triallate. No attempt was made to recover and identify gaseous reaction products.

Table I. Gas Chromatographic Characterization of Triallate Pyrolysis Product Distribution by Integrated Peak Area as a Function of Pyrolysis Temperature[a]

	pyrolysis temp, °C				
compd	475	500	525	550	575
4	2.1	4.2	13.3	40.7	39.6
5	7.9	11.9	29.7	62.6	46.4
6		0.5	2.0	3.5	2.5
7	45.1	59.1	122.6	244.0	168.7
8			0.7	1.3	0.5
9			0.5	1.0	0.5
10			0.8	1.9	0.5
11			0.4	0.9	0.8
12			0.4		0.9
13			0.7	1.3	1.6
14	4.5	2.9	7.6	16.6	13.4
15	3.7	4.5	7.1	7.6	1.0
16		1.8	1.0	4.5	2.2
17			2.5	7.0	8.8
18	6.9	9.8	31.7	27.3	18.9
19					3.2
20	3.7	3.5	4.7	3.4	
21	14.9	22.7	40.9	46.9	21.6
22		0.5	1.2	2.6	2.0
1[b]	851.1 (32)	399.5 (68)	173.9 (86)	98.6 (92)	4.0 (99)

[a] Gas chromatographic conditions described in the Experimental Section. [b] Triallate percent conversion given in parentheses.

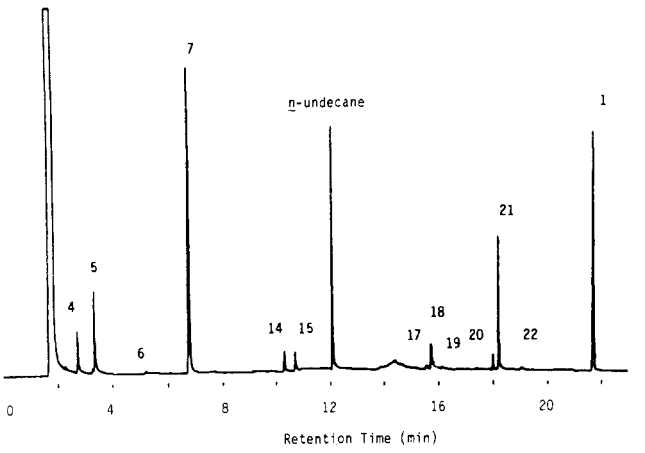
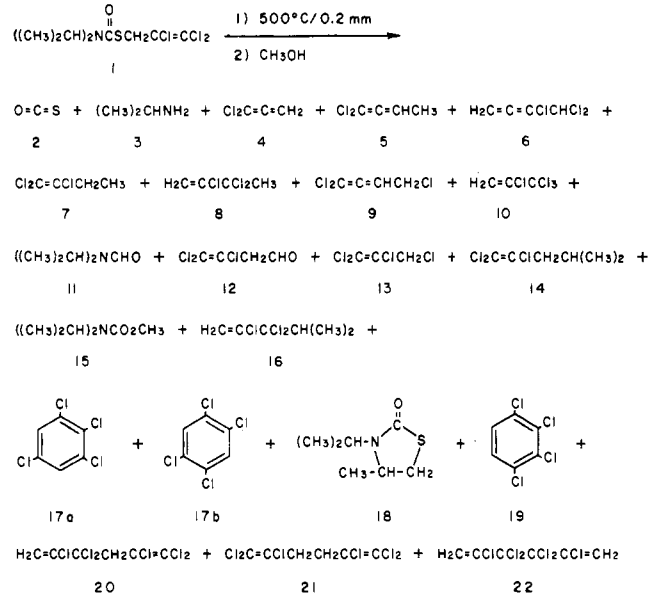


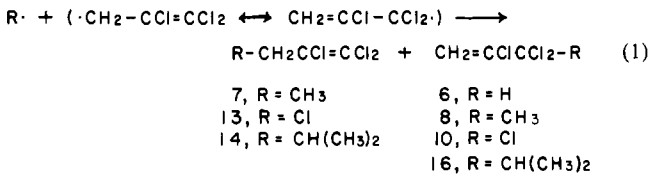
Figure 1. Gas chromatogram of a methanol soultion of triallate pyrolysis (525 °C) product mixture. Compounds are identified in the text. Gas chromatography conditions are described in the Experimental Section.

Identification of Pyrolysis Products. Triallate pyrolysates were analyzed by capillary gas chromatography–mass spectrometry (GC–MS). Product identifications are based on analysis of the resulting mass spectra (Experimental Section). Interpretation of product mass spectra was considerably simplified by assuming that structural features of triallate were also present to a certain extent in the products. Attempts to resolve the components of the pyrolysate by column chromatography for additional NMR and IR analyses were not entirely successful. The structures of the pyrolysis products are shown in Scheme I.

Scheme I

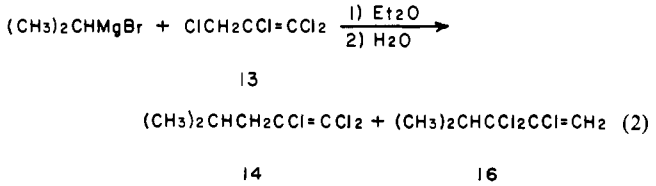


The mass spectra of compounds **6–8**, **10**, **13**, **14**, and **16** suggested that the compounds were derived from the 1,1,2-trichloroallyl portion of triallate by addition of atoms or radicals to a 1,1,2-trichloroallyl radical (eq 1). Radical

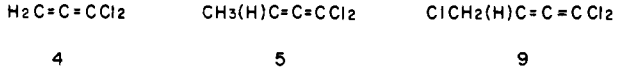


coupling with either end of the 1,1,2-trichloroallyl radical explains the existence of isomeric compounds with the same empirical formulas in the pyrolysis mixture. The mass spectra of **6**, **8**, **10**, and **16** also showed substituted dichloromethyl ions (CCl_2R^+). The absence of these ions in the mass spectra of **7**, **13**, and **14** was the basis for differentiating the two sets of isomers. The identity of compound **13** was verified by GC–MS analysis of an authentic sample.

Several attempts were made to independently synthesize compounds **7**, **8**, **14**, and **16**. Attempts to synthesize **7** by reaction of methyl lithium, methylmagnesium iodide, or lithium dimethylcuprate with **13** were unsuccessful. Reaction of isopropylmagnesium bromide with **13** yielded two compounds that had mass spectra identical with the mass spectra of **14** and **16** (eq 2). Reactions of Grignard reagents and allylic halides frequently yield mixtures of S_N2 and S_N2' products (DeWolfe and Young, 1956).

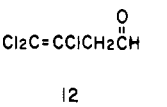


Compounds **4**, **5**, and **9** are 1,1-dichloro-1,2-allenes. Their mass spectra were similar to those reported for other chloroallenes (Kuehl et al. 1980; Stammann et al., 1980).

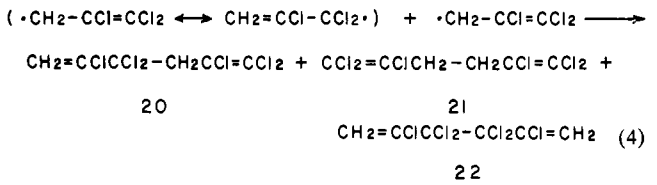


Compounds **11** and **12** contained the diisopropylcarbamoyl functional group. Compound **11** and *N*,*N*-diisopropylacetamide undergo the same spectral fragmentation reactions except for differences due to the formyl group (Kostyanovsky et al., 1973). Compound **15** is an artifact of the methanol workup. It was not present when the pyrolysis mixture was taken up in hexane or methylene chloride. Diisopropylcarbamyl chloride (**23**), the probable pyrolysis product, reacts with methanol to form **15** during the workup (eq 3). Compound **23** was not observed when a hexane solution of the pyrolysate was subjected to GC–MS analysis.

Compound **12** is 3,4,4-trichloro-3-butenal. The 1,1,2-trichloroallyl cation was the most prominent high-mass fragment ion in the mass spectrum of **12**. This cation is due to an [M – 29] fragmentation and indicates loss of a hydrogen atom and carbon monoxide from the molecular ion.

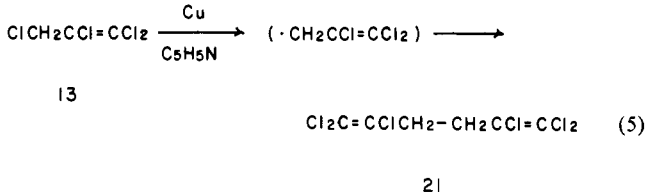


The mass spectra of compounds **20–22** suggested that they were formed by tail-to-head, head-to-head, and tail-to-tail coupling of two 1,1,2-trichloroallyl radicals (eq. 4). Additional minor $C_6H_4Cl_6$ pyrolysis products were



observed, but these products must correspond to isomers with different chlorine atom substitution patterns. These minor products were not identified.

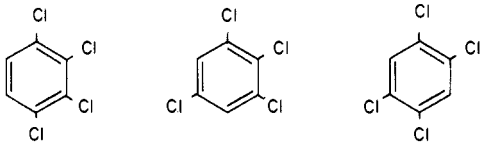
The structural assignment for **21** was confirmed by preparing 1,1,2-trichloroallyl radicals from **13** and observing the coupling products (Dolbier and Harmon, 1971). Sonication of **13** in the presence of copper powder and pyridine yielded a compound with a mass spectrum identical with the mass spectrum of **21** (eq 5). Distributions



of chlorinated allyl radical coupling products similar to those observed in the triallate pyrolysate have been observed in the copper-promoted coupling of 3,3,3-trichloropropene (Dolbier and Harmon, 1971). Coupling of the intermediate 1,1-dichloroallyl radical occurred preferentially at the hydrogen-substituted end of the radical rather than the chlorine-substituted end.

Tetrachlorobenzenes **17** and **19** were minor pyrolysis products. 1,2,3,4-Tetrachlorobenzene (**19**) was identified

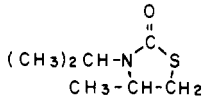
by comparison of its mass spectrum with a mass spectrum



19 17a 17b

of an authentic sample and by gas chromatographic retention time and co-injection studies. The mass spectra of authentic samples of 1,2,3,5-tetrachlorobenzene (**17a**) and 1,2,4,5-tetrachlorobenzene (**17b**) were not sufficiently different to identify **17**. Both isomers had identical retention times under our analysis conditions.

Compound **18** was the only pyrolysis product that could not be conclusively identified from its mass spectrum. Compound **18** was isolated by column chromatography, examined by IR, ^1H NMR, and ^{13}C NMR, and identified as 4,5-dihydro-3-isopropyl-4-methylthiazolidin-2(3*H*)-one (Kashman et al., 1980).



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Product Quantitation and Effect of Pyrolysis Temperature. Pyrolysates were analyzed by capillary gas chromatography using an instrument equipped with a flame ionization detector. Integrated peak areas were measured for each product, but response factors for the majority of the products were not available. Pyrolysis mixtures were quantified by pyrolyzing a constant amount of triallate and adding a constant amount of an internal standard to the pyrolysis mixture. Yields are reported as ratios of the area of a product peak to the area of an undecane internal standard peak (Table I). This procedure permitted comparisons of changes in the product distribution as a function of pyrolysis temperature. The response factor for triallate was determined and was used for calculating triallate conversions as a function of pyrolysis.

Triallate conversions at less than 500 °C were low (Table I), and compounds **7** and **21** were the major products (Table I). Compounds **4**, **5**, **14**, **15**, **18**, and **20** were minor products. Increasing the pyrolysis temperature increased triallate conversions and the quantity of initial products. Triallate conversion was essentially complete at 575 °C, and a broad spectrum of minor products was produced. The complexity of the high-temperature pyrolysis mixture is due to higher concentrations of products formed by minor reaction pathways and secondary thermal reactions of the initially formed thermal reaction products.

The reaction network linking secondary reaction products to the primary reaction products could not be determined directly by pyrolyzing samples of the pyrolysis products because most of the products were not isolated and purified. The structures of **6–8**, **10**, **13**, **14**, **16**, and **20–22** indicated that they were probably primary pyrolysis products. These compounds are formed by combination of the 1,1,2-trichloroallyl radical and other radicals resulting from the fragmentation of triallate. Tetrachlorobenzenes **17** and **19** are probably secondary pyrolysis products arising from the cyclization and aromatization of **20–22**.

The dichloroallenes **4** and **5** were surprising products. Dichloroallene **5** is probably a secondary pyrolysis product formed by hydrogen chloride loss from **7** (eq 6). The yields

$$Cl_2C{=}CClCH_2CH_3 \longrightarrow HCl + Cl_2C{=}C{=}CHCH_3 \quad (6)$$

7 5

of **7** and **5** increased with increasing pyrolysis temperatures, but the yield of **5** increased at a faster rate. This relationship between the yields of **5** and **7** as a function of pyrolysis temperature would be expected if **5** is a pyrolysis product of **7**. Allene **4** could be derived from **6** via a similar thermal hydrogen chloride elimination. However, the ratio of **5** to **4** increased with increasing pyrolysis temperature. If **5** and **4** were formed by similar hydrogen chloride eliminations, the activation energies for the two eliminations should be similar. The change in the **5** to **4** ratio with temperature indicates that **5** and **4** are formed by different mechanisms with different activation energies. Allene **4** could be formed by loss of a chlorine atom from the 1,1,2-trichloroallyl radical (eq 7). Allenes have been ob-

$$\cdot CH_2{-}CCl{=}CCl_2 \longrightarrow CH_2{=}C{=}CCl_2 + Cl\cdot \quad (7)$$

4

served in pyrolyses of allylic and vinyl chlorides (Kunichika et al., 1969; Taylor et al. 1952). Allyl radicals formed in the initial step of allyl iodide pyrolysis yield allene by a complex mechanism (Kunichika et al. 1971).

Reaction Mechanism. The major triallate thermal reaction products indicate that the predominant mode of reactivity is homolytic cleavage of the allylic carbon–sulfur bonds to yield resonance-stabilized 1,1,2-trichloroallyl radicals and diisopropylthiocarbamoyl radicals (eq 8).

$$((CH_3)_2CH)_2NC(=O)S{-}CH_2CCl{=}CCl_2 \longrightarrow ((CH_3)_2CH)_2NC(=O)S\cdot + \cdot CH_2CCl{=}CCl_2 \quad (8)$$

Homolysis of the allylic carbon–sulfur bond rather than the carbonyl carbon–sulfur bond is analogous to the reactivity observed for allylic esters and oxalates (Louw, 1971; Louw and Kooyman, 1967). Most of the observed pyrolysis reaction products are derived from these two radicals or from subsequent reactions of these radicals.

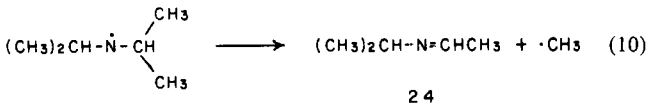
Dimerization of the 1,1,2-trichloroallyl radical yields **20–22** (eq 4). The 1,1,2-trichloroallyl radical also reacts with other radicals present in the hot zone to yield **6–8**, **10**, **13**, **14**, and **16** (eq 1). The radical coupling products show preferential coupling with the least substituted end of the 1,1,2-trichloroallyl radical. Similar selectivity in radical coupling is also observed in reactions of alkyl radicals with alkyl-substituted allyl radicals (Martens et al., 1972; Baulch et al., 1979).

Products due to dimerization of the diisopropylthiocarbamoyl radical or reaction of the diisopropylthiocarbamoyl radical with other radicals present in the hot zone were not observed in any of the triallate pyrolysis mixtures. The diisopropylthiocarbamoyl radical must undergo radical fragmentation reactions faster than radical coupling. The major pyrolysis product, **7**, arises from combination of a methyl radical and the 1,1,2-trichloroallyl radical. Methyl radicals are produced by two sequential fragmentations of the diisopropylthiocarbamoyl radical. The first fragmentation of the diisopropylthiocarbamoyl radical yields carbon oxysulfide (**2**) and the diisopropylamino radical (eq 9). Decarboxylation is characteristic

$$((CH_3)_2CH)_2N{-}C(=O){-}S\cdot \longrightarrow ((CH_3)_2CH)_2N\cdot + O{=}C{=}S \quad (9)$$

2

of carboxyl radicals and is expected to occur readily with the diisopropylthiocarbamoyl radical. This fragmentation explains the origin of the carbon oxysulfide in the pyrolysate mixture. The diisopropylamino radical rapidly fragments to produce a methyl radical and the isopropylimine of acetaldehyde **24** (eq 10). Cleavage of amino

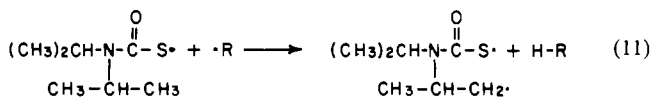


(10)

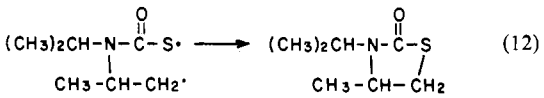
24

radicals to imines is frequently observed at elevated temperatures and has been observed for the diisopropylamino radical (Gowenlock and Snelling, 1962). This imine was not observed in any of the triallate pyrolysis mixtures in spite of extensive efforts. Presumably most of the imine polymerizes to nonvolatile substances. The isopropylamine **3** observed might be due to adventitious hydrolysis of the imine during the workup.

The mechanism for formation of **18** is not clear. It is tempting to suggest that **18** is formed in a sequence involving hydrogen abstraction from a methyl group of the diisopropylthiocarbamoyl radical by some other radical (eq 11). The resulting diradical then cyclizes to **18** (eq 12).

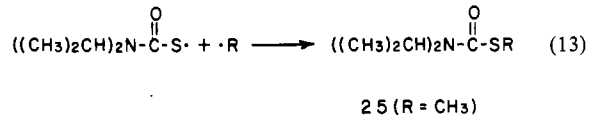


(11)



(12)

This sequence requires high preference for the hydrogen-abstraction reaction compared to coupling of the radical with the diisopropylthiocarbamoyl radical (eq 13). None



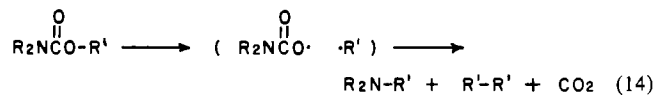
(13)

25 (R = CH_3)

of the possible radical coupling products, such as **25**, containing the diisopropylthiocarbamoyl functional group were observed. Thiocarbamate *S*-ester products analogous to **25** (R = isopropyl) might show high thermal reactivity and be completely lost in secondary pyrolysis reactions, but the methyl coupling product **25** should be sufficiently stable to partially escape secondary pyrolysis reactions and be detected in the pyrolysate.

CONCLUSIONS

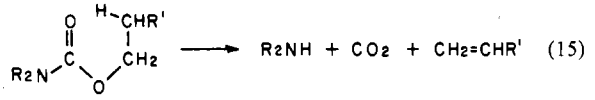
The triallate thermal reaction products resemble the thermal reaction products observed from pyrolysis of *N,N*-dialkylcarbamates that do not contain a β-alkyl carbon–hydrogen bond in the ester portion of the molecule (Adams and Baron, 1965). The product distribution in the pyrolysis of *N,N*-dialkylcarbamates is controlled by the reactions of the initially formed radicals (eq 14). Pyrol-



(14)

ysates will be more complicated than shown in eq 14 if the initially formed radicals undergo additional fragmentation reactions in competition with coupling reactions. The complexity of the triallate pyrolysate is due to the additional fragmentation reactions of the initially formed radical pair. Benthiocarb and diallate do not have β-alkyl carbon–hydrogen bonds and should demonstrate this type of thermal reactivity.

N,N-Dialkylcarbamates with a β-alkyl carbon–hydrogen bond in the ester portion of the molecule undergo concerted elimination of an alkene upon pyrolysis (eq 15).



(15)

N,N-Dialkylcarbamic acids formed in the elimination readily decompose to carbon dioxide and the amine. *S*-Alkyl *N,N*-dimethylthiocarbamates undergo the corresponding thermal reaction (Johnson et al., 1987). Butylate, cycloate, and molinate have β-alkyl carbon–hydrogen bonds and should show this type of thermal reactivity.

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Registry No. **1**, 2303-17-5; **2**, 463-58-1; **4**, 108562-60-3; **5**, 108562-61-4; **6**, 37077-84-2; **7**, 42860-89-9; **8**, 39083-23-3; **9**, 58679-08-6; **10**, 16500-91-7; **11**, 2700-30-3; **12**, 108562-62-5; **13**, 10436-39-2; **14**, 108562-63-6; **15**, 31603-49-3; **16**, 108562-64-7; **18**, 108562-65-8; **19**, 634-66-2; **20**, 97985-58-5; **21**, 98141-62-9; **22**, 108562-66-9; isopropyl bromide, 75-26-3; 1,1,2,3-tetrachloropropene, 10436-39-2.

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