alkylarylstannanes is such a method. The corresponding versatility of the trialkylvinylstannanes has been less well defined. In the present study we have clearly demonstrated that a polyfunctional precursor, the (*E*)-21-(tri-*n*-butylstannyl)-(17α)-19-norpregna-1,3,5(10),20-tetraene-3,17β-diol, which can be prepared in good yields with the defined *E* stereochemistry, undergoes facile ipso substitution with a variety of electrophiles. These reactions which include protonation, deuteriation, halogenation, and phenylselenation proceed at ambient temperatures or lower, within 1–30 min, except in the case of the phenylselenation. In all cases a single product resulting from ipso substitution is obtained in isolated yields of 76–97%. The compounds could be identified by the mass spectra which provided the parent ions, and the stereochemistry could be clearly assigned as the basis of the vinylic coupling constants. No evidence of electrophilic reactions of electrophilic reactions on the unprotected phenolic A ring could be detected. This supports our selection of the trialkylstannyl moiety for activation of sp^2 carbon bonds toward electrophilic substitution in the development of radiopharmaceuticals labeled with the radionuclides of hydrogen, selenium, bromine, or iodine.

Experimental Section

General Methods. IR spectra were obtained via a Perkin-Elmer Model 599B infrared spectrophotometer. ^1H and ^{13}C NMR spectra were taken at ambient temperature in $CDCH_3$, CD_3CO-CH_3, or CD_3OD, with tetramethylsilane as an internal standard on a Varian 300-MHz instrument. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone ketyl. Flash chromatography employed silica gel (230–400 mesh) as the absorbent. Thin layer chromatography was performed on both normal (silica gel) and reverse phase (C-18) plates using chloroform/ethyl acetate (9:1) and ethanol/water (9:1) as the eluents. The *n*-butyllithium, trifluoroacetic acid, trifluoroacetic anhydride, deuterium oxide, diphenyl diselenide, iodine, and bromine were obtained commercially from Aldrich Chemical Co. and used without further purification.

(17α,20*E*)-21-(Tri-*n*-butylstannyl)-19-norpregna-1,3,5(10),20-tetraene-3,17-diol (1). This compound was synthesized from estrone and (*E*)-1,2-bis(tri-*n*-butylstannyl)ethene according to the procedure of Hanson et al:[6] ^1H NMR ($CDCl_3$) δ 0.67–2.67 (41, H, m, steroid nucleus plus $(n\text{-}C_4H_9)_3$, 2.67–2.93 (3 H, m), 6.12 (d, J = 20 Hz, 1 H, C_{21}-H, 6.25 (d, J = 20 Hz, 1 H, C_{20}-H) 6.55 (d, J = 3 Hz, 1 H, C_4-H), 6.70 (d, J = 8 Hz, J = 3 Hz, 1 H, C_2-H), 7.15 (d, J = 8 Hz, C_1-H); MS (EI), m/e 530 ($M^+ - C_4H_9$).

(17α,20*E*)-19-Norpregna-1,3,5(10),20-tetraene-3,17-diol (2). To a suspension of 1 (100 mg, 0.17 mmol) in THF at 0 °C was added dropwise a solution of CF_3CO_2H in THF. The resulting solution was stirred at 0 °C for 30 min, then quenched with 7 N methanolic KF, and neutralized by the addition of 6 N aqueous sodium hydroxide. The reaction mixture was extracted with ethyl acetate; the organic layer was washed sequentially with water and saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. The residue was purified by flash chromatography on silica gel using dichloromethane–ethyl acetate (9:1) as the solvent. The product was obtained in 95% yield (50 mg, 0.16 mol): TLC SiO_2 = 0.29, C-18 = 0.73; ^1H NMR (CD_3OD) 0.95 (5, 3 H, C_{18}-H), 1.24–2.50 (m, 11 H, steroid nucleus), 2.75–2.78 (m, 3 H, C_6-H, C_{10}-H), 5.09–5.19 (m, 2 H, C_{21}-H), 6.06–6.12 (m, 1 H, C_{20}-H), 6.47 (d, J = 3 Hz, C_4-H) 6.55 (dd, J = 8 Hz, J = 3 Hz, 1 H, C_2-H), 7.09 (d, J = 8 Hz, 1 H, C_1-H); ^{13}C NMR (CD_3OD) 14.4, 23.88, 27.19, 28.37, 30.35, 33.02, 36.01, 40.72, 44.58, 47.76, 50.10, 84.63, 113.30, 115.63, 126.76, 132.15, 138.34, 144.18, 155.20 ppm; mass spectrum (EI) m/e 298 (M^+).

(17α,20*E*)-21-Deuterio-19-norpregna-1,3,5(10),20-tetraene-3,17-diol (3). To a suspension of trifluoroacetic anhydride (3.84 mmol, 13.6 mmol) in 5 mL of THF at 0 °C was added deuterium oxide (0.54 mL, 13.6 mmol). The resulting solution was added to a THF solution containing the vinylstannane 1 (0.200 g, 0.34 mmol). The reaction proceeded as for 2. The product was isolated in a 90% yield as a white solid (0.092 g, 0.31 mmol): TLC SiO_2 = 0.29, C-18 = 0.73; ^1H NMR (CD_3OD) δ 0.96 (s, 3 H, $C_{18}H_3$), 1.45–2.50 (m, 11 H, steroid nucleus), 2.75–278 (m, 3 H) 3.3 (s, 1 H), 5.18 (d, J = 17 Hz, C_{21}-H), 6.08 (d, J = 17 Hz, C_{20}-H), 6.55 (d, J = 3 Hz, C_4-H), 6.62 (dd, J = 3 Hz, J = 8 Hz, C_2-H), 7.10 (d, J = 8 Hz, C_1-H); ^{13}C NMR (CD_3OD) 14.53, 23.90, 27.12, 28.30, 30.37, 33.01, 36.04, 40.47, 44.60, 47.25, 49.50, 84.71, 113.33, 115.76, 126.86, 131.28, 138.48, 143.83, 155.23 ppm; mass spectrum (EI), m/e 299 (M^+).

(17α,20*E*)-21-Bromo-19-norpregna-1,3,5(10),20-tetraene-3,17-diol (5). To a solution of 1 (0.100 g, 0.17 mmol) in CCl_4 was added dropwise a 0.02 M solution of bromine in CCl_4 until the color of bromine persisted. To the reaction mixture was added 1 mL of 7 N KF in methanol and 1 mL of a 5% aqueous sodium bisulfate solution. The mixture was extracted with ether, and the organic phase was dried over $MgSO_4$ (anhydrous), filtered, and evaporated to dryness. The residue was purified by column chromatography on silica gel using dichloromethane/ethyl acetate (9:1) as the solvent. The product was isolated as a white solid in a 90% yield (0.058 g, 0.15 mmol): TLC SiO_2 = 0.35; C-18 = 0.69; ^1H NMR (CD_3OD–$CHCl_3$) δ 0.96 (s, C_{18}-H), 1.24–2.43 (m, 11 H, steroid nucleus), 2.75–2.78 (m, 3 H), 3.3 (s, 1 H), 6.24 (d, J = 14 Hz, C_{21}-H), 6.45 (d, J = 14 Hz, C_{20}-H), 6.51 (d, J = 3 Hz, C_4-H, C_2-H, C_1-H, 6.63 (dd, J = 8 Hz, J = 3 Hz, C_2-H), 7.10 (d, J = 8 Hz, C_1-H); ^{13}C NMR (CD_3OD–$CDCl_3$) 14.32, 23.69, 26.96, 28.10, 30.22, 33.07, 36.39, 40.30, 44.37, 47.77, 50.02, 85.61, 113.26, 115.69, 126.80, 130.08, 138.39, 143,50, 155.09 ppm; mass spectrum (EI), m/e 376,374 (M^+) 1:1 for Br isotopes.

(17α,20*E*)-21-(Phenylseleno)-19-norpregna-1,3,5(10),20-tetraene-3,17-diol (6). To a solution of diphenyl diselenide (0.120 g, 0.38 mmol) in THF was added 0.34 mmol of bromine in THF. The solution, which turned from yellow to brown upon formation of the phenylselenenyl bromide, was added dropwise to a solution of the vinylstannane 1 (0.150 g, 0.25 mmol) in THF at 0 °C. The reaction turned green as it was stirred at 0 °C for 5 h. The reaction was quenched by the addition of 7 N aqueous KF and extracted with ethyl acetate. The organic phase was washed with saturated NaCl and water, dried over sodium sulfate (anhydrous), filtered, and evaporated to dryness. The residue was purified by column chromatography on silica gel to yield on oil that solidified on standing: yield 76% (0.087 g, 0.19 mmol); TLC SiO_2 = 0.43, C-18 = 0.67; ^1H NMR (CD_3OD) 0.95 (s, C_{18}-H), 1.25-2.40 (m, 11 H, steroid nucleus), 2.70-284 (m, 3 H), 6.23 (d, J = 16 Hz, C_{21}-H), 6.44 (d, J = 3 Hz, C_4-H), 6.47 (dd, J = 3 Hz, J = 3 Hz, C_2-H), 6.60 (d, J = 16 Hz, C_{20}-H), 7.10 (d, J = 8 Hz, C_1-H), 7.21–7.46 (m, 5 H, Se-C_6H_5); ^{13}C NMR (CD_3OD) 14.80, 24.25, 27.60, 28.81, 30.74, 33.65, 36.82, 41.10, 45.20, 49.51, 50.55, 85.98, 113.75, 116.42, 127.23, 128.11, 130.32, 132.47, 133.17, 138.73, 144.09, 155.89 ppm; mass spectrum (EI), m/e 456, 455, 454, 452 (M^+), multiplicity of Se isotopes.

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Registry No. 1, 82123-95-3; 2, 7678-95-7; 3, 108561-03-1; 5, 103924-36-3; 6, 108561-04-2; estrone, 53-16-7; (*E*)-1,2-bis(tri-*n*-butylstannyl)ethene, 14275-61-7.

The Pyrolysis of *S*-Alkyl Dimethylthiocarbamates

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Thiocarbamate herbicides are used extensively worldwide for controlling the growth of undesirable plant species. These herbicides are relatively nonpersistent in the environment, but the preferred mode of degradation is not well established.[1,2] Thermal reactions could be an

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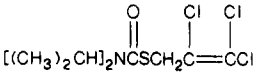
Table I. Pyrolysis Products of *S*-Alkyl Dimethylthiocarbamates [$(CH_3)_2NC(=O)SR$] at 560 °C and 0.15 Torr[a]

compd	R	hydrocarbon products[b]	thiocarbamate conv, %[c]	total recov, %[d]
4	1-octyl	1-octene (100)	14	95
5	1-dodecyl	1-dodecene (100)	11	98
6	2-octyl	1-octene (43) (*E*)-2-octene (37) (*Z*)-2-octene (16) octane (5)	62	90
7	cyclooctyl	(*Z*)-cyclooctene (100)	93	81
8	cyclododecyl	(*E*)-cyclododecene (77) (*Z*)-cyclooctene (16)	98	94
9	2-phenyl-2-propyl	2-phenyl-2-propene (98) isopropylbenzene (2)	100	89
10[e]	1-octyl	1-octene (100)	96	84

[a] Thiocarbamate conversions, total recoveries, and hydrocarbon product distributions determined gas chromatographically. Each value represents the average of three pyrolyses. [b] Numbers in parentheses represent the hydrocarbon product distribution. [c] Difference between the initial and recovered amounts of the *S*-alkyl dimethylthiocarbamate. [d] Sum of the hydrocarbon products and the recovered *S*-alkyl dimethylthiocarbamate compared to the initial *S*-alkyl dimethylthiocarbamate. [e] *O*-1-Octyl dimethylthiocarbamate.

important degradation mechanism for thiocarbamate herbicides because of weak carbon–sulfur bonds in the functional group.[3] The thiocarbamate herbicide triallate (1) reacts thermally by carbon–sulfur bond homolysis to yield trichloroallyl and diisopropylthiocarbamoyl radicals.[4] Similar reactions might be expected of the thiocarbamate herbicides butylate (2) and vernolate (3). *S*-Alkyl di-



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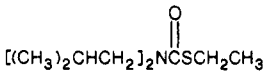

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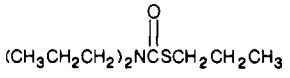

3

methylthiocarbamates contain structural features similar to those in **2** and **3**. Pyrolysis of *S*-alkyl dimethylthiocarbamates should indicate how **2** and **3** will react thermally. Comparison of the pyrolyses of *S*-alkyl dimethylthiocarbamates and *O*-alkyl dimethylthiocarbamates also provides an interesting study of the effects of structural variation on thermal reactivity.

The *S*-alkyl dimethylthiocarbamates **4–9** were most conveniently prepared by the Schotten–Baumann procedure.[5] Other procedures gave lower yields and required greater experimental effort. The products were easily purified by vacuum distillation except for compound **5**, which was purified by recrystallization, and compound **9**, which required column chromatography. No detectable impurities were observed by gas chromatography or in the ^1H NMR spectra of the compounds. *O*-1-Octyl dimethylthiocarbamate (**10**) was prepared by the method of Newman and Hetzel.[6]

Compounds **2–9** were subjected to flash vacuum pyrolysis at 560 °C and 0.15 Torr to yield hydrocarbon products derived from the ester portion of the molecule (Table I). No attempt was made to recover dimethylamine or carbonoxysulfide, the expected products from the amide portion of the molecule. The dimethylammonium salt of dimethylthiocarbamic acid, observed in the pyrolyses of *O*-alkyl dimethylthiocarbamates, was not a pyrolysis product.[6] Products from the pyrolysis of **4** were identified by gas chromatography–mass spectrometry. Hydrocarbon pyrolysis products from the other thiocarbamates were identified by their gas chromatographic retention times and by coinjection studies. Thiocarbamate conversions, total recoveries, and distribution of the hydrocarbon reaction products given in Table I represent the average of at least three pyrolyses. Variations in conversions, recoveries, and hydrocarbon product distributions were on the order of a few percent from run to run.

Pyrolysis of compounds **4–9** yielded alkenes as the major hydrocarbon products (Table I). Small amounts of alkanes were observed from compounds **6** and **9**. The alkene products were the same as those observed from pyrolysis of the corresponding *O*-alkyl dimethylthiocarbamates.[6] The octene mixture obtained from pyrolysis of **6** was substantially richer in 2-alkenes (55%) than has been observed from the pyrolysis of 2-heptyl acetate (46%) but was essentially the same as the octene mixture obtained from the pyrolysis of 2-octyl methylxanthate.[7,8] Pyrolysis of **7** yielded (*Z*)-cyclooctene exclusively, while pyrolysis of **8** yielded a mixture of (*Z*)- and (*E*)-cyclododecenes. Similar results have been observed in the pyrolysis of cyclic acetates and xanthates.[9] Eight-membered and smaller rings yield only the (*Z*)-cycloalkenes, while larger, more conformationally flexible systems yield a mixture of (*Z*)- and (*E*)-cycloalkenes.

Reactivity differences in **4–9** based on the extent of conversion at a constant pyrolysis temperature depended on the structure of the *S*-alkyl group (Table I). Tertiary S-esters were more reactive than secondary S-esters, which were more reactive than primary S-esters. Similar trends in reactivity as a function of ester structure are also observed in the pyrolysis of acetates and xanthates.[10,11] The *S*-alkyl dimethylthiocarbamates are less reactive than the corresponding *O*-alkyl dimethylthiocarbamates. Pyrolysis of **10** at 430 °C resulted in a conversion comparable to that observed for **9** at 500 °C. Primary *O*-alkyl dimethylthiocarbamates have a thermal reactivity slightly less than the thermal reactivity of tertiary *S*-alkyl dimethylthiocarbamates.

The alkene products and the structure–reactivity relationships observed from the pyrolysis of the *S*-alkyl dimethylthiocarbamates are consistent with a concerted

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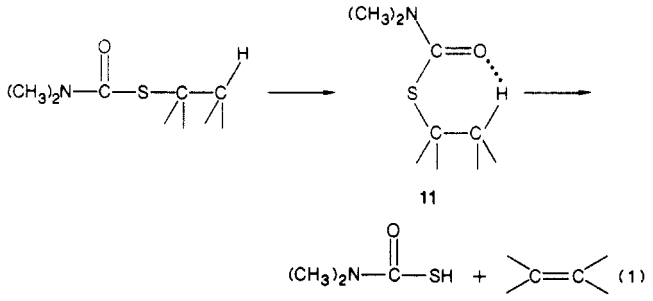
mechanism involving a cyclic, six-membered transition state (11) to yield an alkene and dimethylthiocarbamic acid (eq 1). The dimethylthiocarbamic acid subsequently



11

(1)

decomposes to dimethylamine and carbon oxysulfide.[12] Reactivity differences between acetates and thioacetates are largely due to differences in the polarization of the ester α-carbon by the attached oxygen or sulfur atom.[10] Reactivity differences between thioacetates and dithioacetates are smaller.[10] The differences between a carbonyl or a thiocarbonyl functional group are less important in the transition state leading to elimination. The lower reactivity of **4–9** compared to **10** indicates that sulfur is less able to polarize the α-carbon of the ester than oxygen, resulting in a later transition state. The regioselectivity in the reaction of **6** is also consistent with a later, more product-like transition state. A late, high-energy transition state for elimination and a weak carbon–sulfur bond allows competing homolysis mechanisms in the pyrolyses. Small amounts of alkane products were observed in the pyrolysis of **6** and **9**. Carbon–sulfur bond homolysis mechanisms will become more important in the pyrolysis of *S*-alkyl dimethylthiocarbamates when the structure of the ester portion of the molecule will not allow transition states such as **11**.

Pyrolysis reactions of **2** or **3** are expected to be similar to those observed for the *S*-alkyl dimethylthiocarbamates **4–9**. Alkenes, carbon oxysulfide, and secondary amines should be pyrolysis reaction products.

Experimental Section

All solvents were purified by standard techniques. Hydrocarbon standards, dimethylcarbamoyl chloride, and dimethylthiocarbamoyl chloride purchased from Aldrich Chemical Chemical Company (Milwaukee, WI) were used as received. Cyclooctanethiol and cyclododecanethiol were prepared by reaction of thiolacetic acid with the appropriate alkene followed by hydrolysis.[13] 1-Octanethiol, 2-octanethiol, and 2-phenyl-2-propanethiol were prepared by reaction of thiourea with the appropriate alkyl bromide followed by in situ hydrolysis of the *S*-isothiouronium salt.[14]

Melting points (uncorrected) were obtained with a Thomas Hoover capillary melting point apparatus. ^{1}H NMR spectra were recorded on a Varian Associates EM-390 90-MHz nuclear magnetic resonance spectrometer with carbon tetrachloride and tetramethylsilane. Gas chromatographic analyses were performed with a Varian Associates 3700 gas chromatograph (flame ionization detector) equipped with a 30 m × 0.33 mm DB-1 capillary column (J & W Scientific). The gas chromatograph was interfaced to a Shimadzu Chromatopac C-R3A integrator. Reactants and products were quantified with *n*-undecane with consideration for detector response factors. Gas chromatography–mass spectrometry was performed with a Hewlett-Packard Model 5992-A gas chromatograph–mass spectrometer equipped with a Hewlett-Packard ultra performance, cross-linked methylsilicone fused silica capillary column (25 m × 0.31 mm i.d.). Ionization was by electron impact at 70 eV. Elemental analyses were performed by Desert Analytics (Tuscon, AZ).

Pyrolysis Apparatus. The pyrolysis apparatus consisted of a quartz tube (2.2 cm i.d.) heated by a Model 58914 Lindberg heavy duty furnace. The hot zone was 45 cm long. One end of the pyrolysis tube was connected to a cold trap, which was connected to a vacuum manifold. A sample reservoir was connected to the other end of the pyrolysis tube. Portions of the pyrolysis tube projecting from the furnace were wrapped with heating tape. Pressures were measured at the manifold.

Pyrolysis Procedure. The furnace and pyrolysis tube were brought to the desired temperature. The *S*-alkyl dimethylthiocarbamate (100 mg) was loaded into the sample reservior and melted if solid. The apparatus was assembled, the sample reservoir cooled with liquid nitrogen, and the system evacuated. After 5 min, the trap was cooled with liquid nitrogen, and the sample reservoir was gently warmed with a heat gun to vaporize the sample. Vacuum was maintained for 10 min after no visible traces of sample remained in the sample reservoir. 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. Benzene and a benzene solution of undecane were added to the trap. This solution was immediately analyzed by gas chromatography.

General Procedure for Synthesis of *S*-Alkyl Dimethylthiocarbamates. A solution of 20% NaOH (20 mL) and thiol (53.8 mmol) was mechanically stirred at 0 °C. Dimethylcarbamoyl chloride (4.95 mL, 53.8 mmol) was added dropwise over 45 min. The solution was allowed to warm to room temperature and extracted with ether (2 × 50 mL). The combined ether extracts were washed with water (50 mL) and brine (2 × 50 mL) and then dried over $MgSO_4$. The solution was filtered and the ether removed on a rotary evaporator. The residual oil was vacuum distilled to yield pure *S*-alkyl dimethylthiocarbamate. Compounds **5**, **8**, and **9** were obtained as slightly impure oils. Compounds **5** and **8** were crystallized from ethanol. Compound **9** was purified by column chromatography (silica gel/pentane) followed by recrystallization from ethanol.

4: bp 110 °C (5 Torr); ^{1}H NMR δ 2.97 (s, 6 H), 2.80 (t, 2 H), 1.27 (m, 12 H), 0.87 (t, 3 H). Anal. Calcd for $C_{11}H_{23}NOS$: C, 60.78; H, 10.66. Found: C, 61.18; H, 11.03.

5: mp 39–41 °C (ethanol); ^{1}H NMR δ 3.0 (s, 6 H), 2.89 (t, 2 H), 1.25 (m, 20 H), 0.87 (t, 3 H). Anal. Calcd for $C_{15}H_{31}NOS$: C, 65.88; H, 11.42. Found: C, 66.13; H, 11.73.

6: bp 92–97 °C (4 Torr); ^{1}H NMR δ 3.48 (m, 1 H), 2.93 (s, 6 H), 1.57–1.27 (m, 13 H), 0.88 (t, 3 H). Anal. Calcd for $C_{11}H_{23}NOS$: C, 60.78; H, 10.66. Found: C, 61.23; H, 10.91.

7: bp 130 °C (4 Torr); ^{1}H NMR δ 3.56 (pentet, 1 H), 2.98 (s, 6 H), 1.37 (m, 14 H). Anal. Calcd for $C_{11}H_{21}NOS$: C, 61.35; H, 9.82. Found: C, 61.40; H, 9.98.

8: mp 43–45 °C (ethanol); ^{1}H NMR δ 3.57 (pentet, 1 H), 2.93 (s, 6 H), 1.37 (m, 22 H). Anal. Calcd for $C_{15}H_{29}NOS$: C, 66.37; H, 10.77. Found: C, 66.19; H, 10.95.

9: mp 56–58 °C (ethanol); ^{1}H NMR 7.6–7.07 (m, 5 H), 2.80 (s, 6 H), 1.85 (s, 6 H). Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.54; H, 7.67. Found: C, 64.54; H, 7.94.

Acknowledgment. We thank Mark Carlson of the U.S.D.A. Metabolism and Radiation Research Laboratory, Fargo, ND, for performing the GC–MS analyses. We acknowledge financial support from the North Dakota Water Resources Research Institute and the U.S. Geological Survey.

Registry No. **4**, 108346-88-9; **5**, 108346-89-0; **6**, 108346-90-3; **7**, 108346-91-4; **8**, 108346-92-5; **9**, 108346-93-6; **10**, 21299-35-4; dimethylcarbamoyl chloride, 79-44-7; 1-octyl mercaptan, 111-88-6; 1-dodecyl mercaptan, 112-55-0; 2-octyl mercaptan, 3001-66-9; cyclooctanethiol, 20628-54-0; 2-phenyl-2-propyl mercaptan, 16325-88-5; 1-octene, 111-66-0; 1-dodecene, 112-41-4; (*E*)-2-octene, 13389-42-9; (*Z*)-2-octene, 7642-04-8; (*Z*)-cyclooctene, 931-87-3; (*E*)-cyclododecene, 1486-75-5; 2-phenyl-2-propene, 98-83-9.

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