Kinetics and mechanism of the pyrolysis of diallyldimethylsilane

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2210 *Organometallics* **1985**, *4*, 2210–2213

135 (15), 122 (26), 121 (12), 119 (14), 117 (10), 109 (18), 107 (28), 105 (16), 95 (11), 93 (16), 89 (13), 87 (10), 81 (11), 79 (12), 77 (10), 74 (12), 73 (100), 67 (11), 59 (21), 55 (13), 53 (19), 45 (44), 44 (14), 43 (45). Anal. Calcd for $C_{10}H_{19}ClGeSi$: C, 43.61; H, 6.95. Found: C, 43.88; H, 7.08.

1,1-Bis(chlorodimethylgermyl)cyclopentadiene, 12. A solution of 1.47 g (8.47 mmol) of Me_2GeCl_2 in 5 mL of THF was placed in a 50-mL flask equipped with a magnetic stirring bar, argon inlet, septum, and a reflux condenser. The solution was cooled by using an ice-water bath, and 10 mL of an 0.4 M solution of lithium (trimethylsilyl)cyclopentadienide in THF was added by using a syringe. The mixture was stirred at room temperature for 42 h and refluxed for 3 h. After removal of most of the solvent under reduced pressure, the salts were precipitated by adding 15 mL of hexane, separated by centrifugation, and washed with three 5-mL portions of hexane. The combined organic portions were distilled by using a 15-cm column packed with glass beads. The major fraction, bp 60–70 °C at 0.05–0.06 torr, contained 0.13 g (12% isolated yield) of 11 and 0.55 g (40% isolated yield) of 12. ^1H NMR ($CDCl_3$): δ 0.61 (s) 12 H, $GeMe_2$; 6.5–7.0 (m) 4 H, vinylic protons. ^{13}C NMR ($CDCl_3$, -10 °C[13]): δ 3.53 (q), GeMe; 60.1 (s) allylic; 132.6 (d) and 133.8 (d), vinylic. MS: *m/z* (relative intensity) 342 (1.5), 340 (1.6), 338 (1.2), 170 (22), 169 (11), 168 (100), 167 (29), 166 (74), 164 (56), 153 (18), 151 (16), 149 (13), 141 (12), 139 (29), 137 (25), 135 (16), 111 (12), 109 (22), 107 (17), 105 (11), 89 (16), 87 (12), 77 (15). Anal. Calcd for $C_9H_{16}Cl_2Ge_2$: C, 31.73; H, 4.85. Found: C, 31.76; H, 4.74.

General Procedure for the Lithium Chloride Catalyzed Cleavage Reactions. The reaction of 5 with lithium chloride is given as a typical example. A Pyrex tube was charged with 25.3 mg (0.60 mmol) of LiCl which was dried by heating with a flame under high vacuum, ca. 0.05 torr. After the solution was cooled, a magnetic stirring bar, 4.0 mL of THF, 250 μL (2.05 mmol) of Me_2SiCl_2, and 0.463 g (2.01 mmol) of 5 were added under nitrogen. The tube was degassed and sealed. After 13 h the tube was opened (experiment 2) and the contents were analyzed by GLC using an internal standard method. The starting silane 5 was 82% reacted, and the absolute yields of 7 and Me_3SiCl were 65% and 73%, respectively.

The details and results of these experiments are summarized in Table I. In all of the experiments product identities were confirmed by comparison of GLC retention times, GC/MS, and ^1H NMR with those authentic samples. No reaction was observed in the absence of LiCl (experiments 1 and 9) or with bis(trimethylsilyl)cyclopentadiene, 8 (experiment 8).

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Registry No. 3, 78133-11-6; 4, 96502-50-0; 5, 96502-49-7; 6, 98991-12-9; 7, 53212-72-9; 9, 98991-13-0; 10, form a, 78921-94-5; 10, form b, 79317-67-2; 11, 98991-14-1; 12, 98991-15-2; $C_5H_5SiMe_3$, 25134-15-0; Me_2SiCl_2, 75-78-5; $C_5H_5GeMe_3$, 26168-12-7; Me_2GeCl_2, 1529-48-2; LiCl, 7447-41-8; Me_3GeCl, 1529-47-1; lithium (trimethylsilyl)cyclopentadienide, 76514-39-1.

Kinetics and Mechanism of the Pyrolysis of Diallyldimethylsilane

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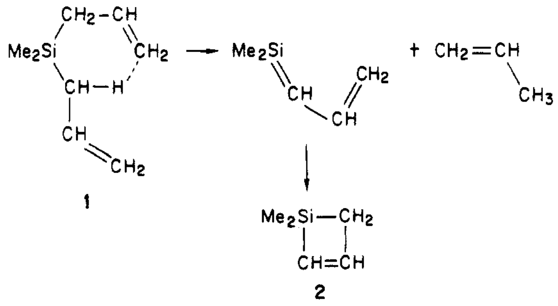
A gas-kinetic study of the pyrolysis of diallyldimethylsilane is described. The main reaction, for which Arrhenius parameters are reported, is the retroene elimination of propene with formation of a silacyclobutene; there are also extensive secondary reactions which are explained by analogy with the pyrolysis of allyltrimethylsilane. Analogies are also drawn with the pyrolysis of related hydrocarbons.

Introduction

While attempting to study silabutadienes, Block and Revelle found that flash vacuum pyrolysis (FVP) of diallyldimethylsilane (1) at 873 K gave mainly propene and 1,1-dimethyl-1-silacyclobutene (2), with some unspecified minor products.[2] Very reasonably, they suggested retroene elimination of propene, followed by cyclization of a transient silabutadiene, as shown in Scheme I.

We are actively interested in gas-kinetic studies of the interplay between molecular and radical pathways in the pyrolysis of organosilicon compounds and of the role of silyl radicals, silenes, and silylenes as intermediates in these pyrolysis mechanisms. By carrying out the first kinetic study of the pyrolysis of allyltrimethylsilane, we were able to show that radical-forming homolysis and a silene-forming retroene reaction were both important primary reactions and that the formation of vinyltrimethylsilane (which had previously prompted controversial mechanistic speculation) was a secondary reaction resulting from radical addition to allyltrimethylsilane.[3] By combining these kinetic studies with deuterium labeling experiments, we have subsequently refined these conclusions to give a

Scheme I



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(1) Visiting from Anorganisch-Chemisches Institüt, Westfälische Wilhems-Universität, 4400 Münster, Federal Republic of Germany.

(2) Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 1630.

(3) Davidson, I. M. T.; Wood, I. T. *J. Organomet. Chem.* **1980**, *202*, C65.

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Table I. Partial Mass Spectra (Approximate Intensities in Arbitrary Units)

compd	*m/e* 140$^+$	125$^+$	112$^+$	99$^+$	98$^+$	97$^+$
1	10	5	1	200	5	10
3	5	10		2	20	2
4	5	5	1	5	15	5
5	5	10	3	15	5	30

wholly satisfactory quantitative description of the course of this complex and interesting pyrolysis.[4] We have also shown from other kinetic experiments[5] that the silabutadiene, $CH_2{=}Si(Me)CH{=}CH_2$, has little more stabilization than the silene, $CH_2{=}SiMe_2$. We now report an investigation of the kinetics and mechanism of the pyrolysis of 1 which follows naturally from the foregoing. Our results are supported by a parallel investigation of the preparative-scale pyrolysis (ca. 100 g) of diallyldimethylsilane.[6]

Experimental Section

Kinetic studies of the pyrolysis of 1 between 772 and 847 K were undertaken by our low-pressure pyrolysis (LPP) technique, with analysis by quadrupole mass sepctrometry.[4] In these experiments the initial pressure of 1 was normally ca. 0.05 torr. To gain further information about products, some pyrolyses were also carried out in a stirred-flow reactor (SFR) with analysis by gas chromatography[7] and in a static system at higher pressure (1–5 torr) with analysis by GC/mass spectrometry.

Results

Products. Propene and 1,1-dimethyl-1-silacyclobutene (**2**) were detected in the mass spectra from the LPP experiments. No other products were identified in these experiments, but in a SFR experiment at 814 K with a partial pressure of 1 of ca. 0.1 torr, peaks with longer retention time than 1 were observed in the gas chromatograph, together with propene and 2. These new peaks (products **3–5**) were also observed in a pyrolysis of 1 for 15 min at 723 K in the static system with analysis by GC/mass spectrometry. Significant features of the mass spectra of products 3–5, and of 1, are in Table I; it is clear that 3–5 are isomers of 1. Other new products were also observed under these conditions, as shown in Table II.

With 5 torr of 1, pyrolyzed for 12 min at 763 K, the wider range of products shown in Table III was obtained, together with ethene and propene, as in Table II. In pyrolyses above 800 K, trace quantities of an isomer of 2 were also detected. This product had a GC retention time similar to the C_5 hydrocarbon products, i.e., shorter than 2, while its mass spectrum had a *m/e* 83$^+$ peak which was ca. 12.5 times more intense relative to *m/e* 98$^+$ than in 2; it may be (trimethylsilyl)acetylene. Other trace products, with molecular weights of 170 and 156, may be cyclic silanes containing two silicon atoms. Even more products were observed in a preparative-scale pyrolysis of 1 at 980 K (the conditions favored by Block and Revelle[2]), while pyrolysis of 2 at 890 K likewise gave many products. Not surprisingly, extensive pyrolysis of 1 is extremely complex. We shall confine ourselves to considering the mechanistic significance of the main products (Tables II and III) formed in the early stages under relatively mild conditions.

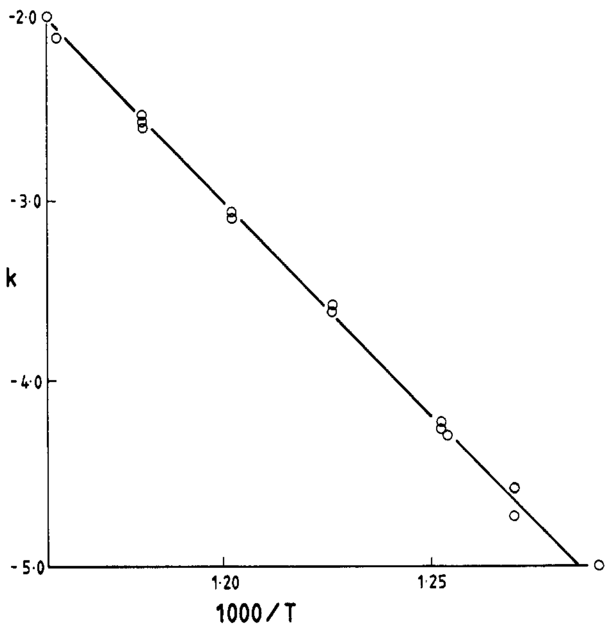

Figure 1. Arrhenius plot for formation of propene from diallyldimethylsilane.

Structural assignments in Tables II and III are based on comparisons of mass spectra and GC retention times with authentic or similar compounds. Where this assignment was not unambiguous, the isomer which we consider to be the most likely is shown.

Diallyldimethylsilane was also pyrolyzed in the SFR with a 10-fold excess of methanol between 851 and 860 K; methanol did not affect the formation of propene, but reduced substantially the formation of 2 and gave a new product with the mass spectrum to be expected for allyldimethylmethoxysilane (peaks at *m/e* 130$^+$, 115$^+$, and 89$^+$ with relative intensities of 1:8:48). In similar experiments with added chloromethane,[4] formation of chlorosilanes did not exceed 1%.

Kinetic Results. As may be seen from Table I, the *m/e* 99$^+$ peak is the most distinctive feature of the mass spectrum of 1; kinetic measurements for the decomposition of 1 were therefore made on the decay of that peak. The decomposition was shown to be first order by varying initial pressure between 0.05 and 1 torr; first-order rate constants were given by $\log A = 10.7 \pm 0.1$ and $E/\text{kJ mol}^{-1} = 192 \pm 2$, but rate constants based on these parameters may be underestimates for the decomposition of 1 because *m/e* 99$^+$ is also a peak in the mass spectrum of product 5. The kinetics of the main reaction forming propene and 2 were monitored by followed the growth of the *m/e* 98$^+$ peak (the molecule ion of 2) and of the *m/e* 38$^+$, 39$^+$, and 41$^+$ peaks (propene fragment ions). Arrhenius parameters based on each of these agreed reasonably well with each other, but the smallest error limits were obtained with *m/e* 41$^+$, which had the best sensitivity factor in our mass spectrometer and suffered the least interference from other ions; that is therefore our best measure of the rate constant for the formation of propene, giving $\log A = 11.2 \pm 0.1$ and $E/\text{kJ mol}^{-1} = 199 \pm 2$. The Arrhenius plot which gave these parameters is in Figure 1.

Discussion

In this work we have confirmed that at low pressure, 1 undergoes pyrolysis to form mainly propene and 2, as found by Block and Revelle;[2] but three isomers of 1, products 3–5, are also formed. It is evident from Tables II and III that the complexity of the pyrolysis increases substantially with increasing pressure of 1, just as was

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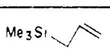
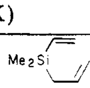
[4] Barton, T. J.; Burns, S. A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Wood, I. T. *J. Am. Chem. Soc.* **1984**, *106*, 6367.

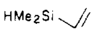
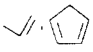
[5] Davidson, I. M. T.; Fenton, A.; Jackson, P.; Lawrence, F. T. *J. Chem. Soc., Chem. Commun.* **1982**, 806.

[6] Ellmann, A. *Dissertation*, Münster, 1985; Auner, N.; Ellmann, A.; Grobe, J., to be submitted for publication.

[7] Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 972.

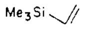
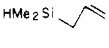
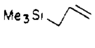
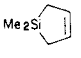
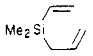
Table II. Products from Pyrolysis of 1 (1 torr at 723 K)

product	C_2H_4	C_3H_6	**2**				**3**	**4**	**5**
approx rel yield	1^a	8^a	5	1	1^b	2^b	3	3	1

products in trace amounts: Me_2SiH_2, Me_3SiH,  

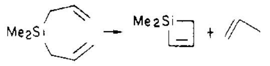
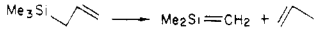
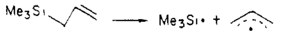
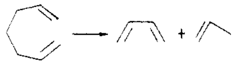
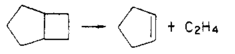
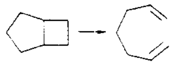
[a] From GC peak areas in the SFR; light hydrocarbons were not quantitatively detected by GC/MS. [b] Or isomer.

Table III. Products from Pyrolysis of 1 (5 torr at 763 K)

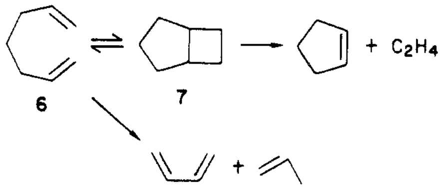
product	Me_3SiH	Me_4Si				**2**		
approx rel yield	1	1	1	1	0.5	5	3	2^b
product						**3**	**4**	**5**
approx rel yield	*a*		*a*, *b*	2^b		3	3	1

[a] Trace quantity. [b] Or isomer.

Table IV. Arrhenius Parameters for Primary Reactions

reaction	temp/K	log *A*	*E*/kJ mol^{-1}	k_{800K}	ref
	772-847	11.2 ± 0.1	199 ± 2	1.61 x 10^{-2}	this work
	863-943	11.6 ± 0.5	230 ± 8	3.82 x 10^{-4}	4
	863-943	15.6 ± 0.5	307 ± 8	3.58 x 10^{-5}	4
	628-742	11.3 ± 0.4	197 ± 3	2.73 x 10^{-2}	8
	699-737	14.8	254	1.64 x 10^{-2}	9
	699-737	15.4	268	7.96 x 10^{-3}	9

Scheme II



found in the pyrolysis of allyltrimethylsilane.[4] An analogy in hydrocarbon chemistry to the low-pressure pyrolysis of 1 is the pyrolysis of hepta-1,6-diene (**6**), which has been shown mainly to undergo retroene decomposition to propene and butadiene, with 4-methylcyclohexene, ethene, and cyclopentene as minor products. Further products, including cycloheptene, were formed at high conversion.[8] The kinetics of pyrolysis of bicyclo[3.2.0]heptane (**7**), an isomer of **6**, have also been studied.[9] It isomerizes to **6** and also decomposes by a biradical route to ethene and cyclopentene, as shown in Scheme II.

Arrhenius parameters for these hydrocarbon pyrolyses,[8,9] and for the primary reactions in the pyrolysis of allyltrimethylsilane,[4] are compared with those of **1** in Table IV.

The Arrhenius parameters for the formation of propene from **1** and **6** are identical within experimental error, confirming the retroene mechanism in Scheme I, with a six-center transition state involving an allylic hydrogen atom. In contrast, the retroene elimination of propene from allyltrimethylsilane involves a hydrogen atom in a methyl group, thus requiring a higher activation energy. Consequently, this process is of minor importance in the pyrolysis of **1**. Likewise, the experiments with added chloromethane show that homolysis to form silyl radicals is a minor process, as would be expected from the kinetic data in Table IV.

Further support for the retroene mechanism comes from the pyrolysis of **1** in excess methanol, in which formation of **2** was suppressed and the methanol adduct of the silabutadiene was observed.

For diallyl compounds, $X(CH_2CH{=}CH_2)_2$, where X = CH_2, O, and NH, the activation energy for retroene elimination of propene decreases from 197 kJ mol^{-1} when X = CH_2 (compound **6**)[8] through 171 kJ mol^{-1} when X is[10] O to 159 kJ mol^{-1} when X is[11] NH. This trend has been taken to be indicative of increasing polarization in the transition state.[10] The fact that **1** and **6** have essentially the same activation energy thus implies that there is little difference in the polarity of the transition states in these two pyrolyses and that nitrogen and oxygen influence the polarity more than silicon does. It may be seen from Table IV that the *A* factor of $10^{11.2}$ s^{-1} found in this work is the same within experimental error as that found for the corresponding decomposition of the hydrocarbon **6** to butadiene and propene; the latter *A* factor is in excellent agreement with a thermochemical kinetic calculation.[8] Likewise, the *A* factor for the retroene elimination of propene from allyltrimethylsilane[4] agrees well with that

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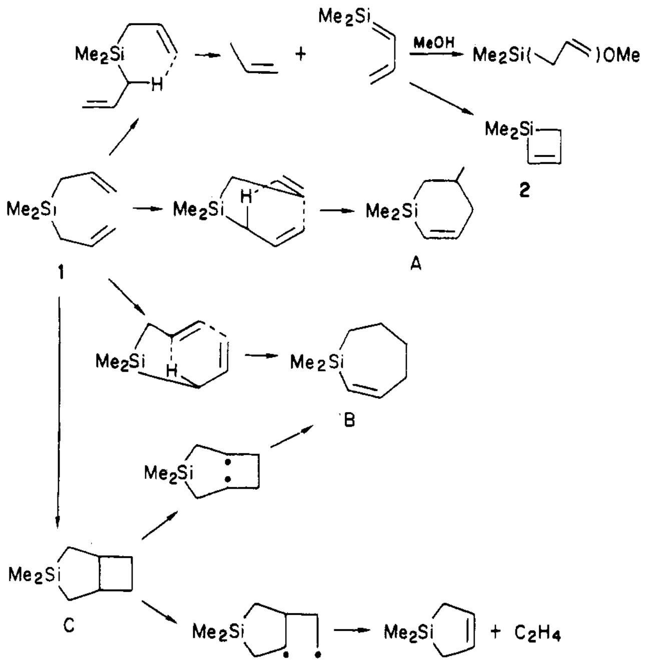
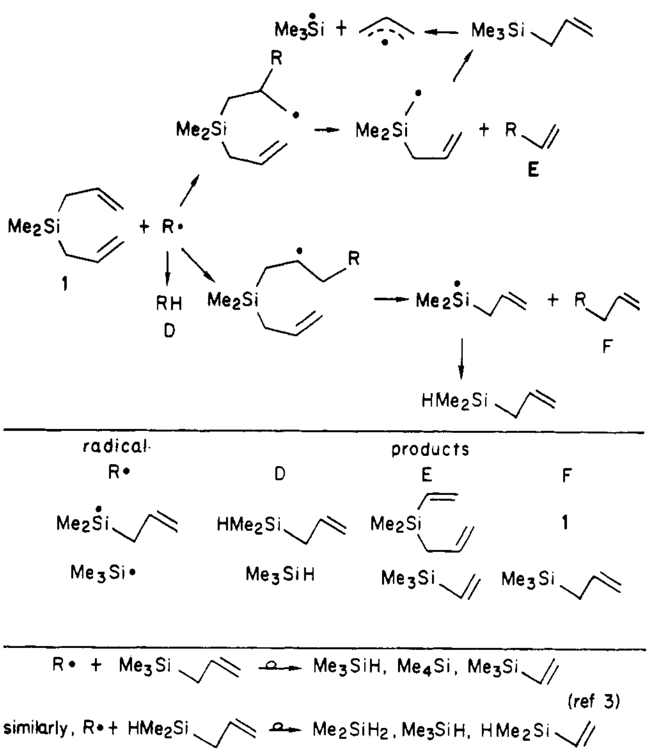
[8] Egger, K. W.; Vitins, P. *J. Am. Chem. Soc.* **1974**, *96*, 2714.
[9] Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 4184.
[10] Vitins, P.; Egger, K. W. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1292.
[11] Egger, K. W.; Vitins, P. *Int. J. Chem. Kinet.* **1974**, *6*, 371.

Scheme III



Scheme IV

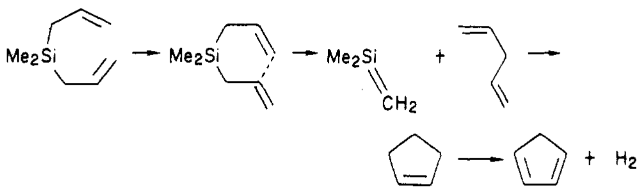


for an analogous hydrocarbon reaction, decomposition of hept-1-ene.[8]

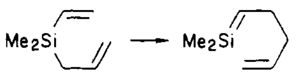
Low-pressure pyrolysis of 1 also produces its isomers 3–5, which are presumably formed in unimolecular primary reactions. A striking feature of Table I is that 3–5 doe not show a prominent m/e 99^+ peak, which is intense in the mass spectrum of 1. The obvious inference is that 3–5 have no free allyl group; they are probably cyclic compounds formed by intramolecular additions. By analogy with the pyrolysis of hydrocarbon 6, likely reactions are shown in Scheme III.

The counterparts to A, B, and C were all observed in the pyrolysis of 6. Product 5, with relatively intense mass spectral peaks at m/e 112^+ and 97^+ (Table I), may be C, but we have insufficient information to match A–C to 3–5.

Although there appears to be a substantial increase in complexity when the pressure of 1 is increased (Tables II and III), formation of most of the new products may be simply explained as arising from radical additions to 1, exactly analogous to the secondary reactions observed in the pyrolysis of allyltrimethylsilane.[4] As already noted, 1 undergoes a retroene reaction much faster than allyltrimethylsilane. Consequently, homogeneous formation of silyl and allyl radicals is relatively much less important in 1 than in allyltrimethylsilane; but minor radical pathways are still feasible, because the secondary reactions in question are chain reactions, only requiring initial formation of a few radicals, which may be formed homogeneously or heterogeneously. The radical reactions in Scheme IV account for all of the products in Tables II and III except the C_5 hydrocarbons. These may result from secondary decomposition of 3–5 or from a minor six-center reaction of 1, thus



It should be noted that the Cope rearrangement undergone by 1,5-dienes would not lead to a stable product from allylvinyldimethylsilane, but to a silene:



The reactions suggested above and in Schemes III and IV are the minimum necessary to explain the formation of the main products. As already noted, the pyrolysis is substantially more complex and many other minor secondary reactions would occur. For instance, some of the cyclic products in Scheme III may also be formed by cyclization of the radicals formed bimolecularly in Scheme IV.

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Registry No. 1, 1113-12-8; 2, 66222-35-3; A, 98858-82-3; B, 98858-83-4; C, 34602-46-5.