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# Synthesis of Two Major Toxaphene Components and Their Photostabilities

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The synthesis of 2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,9,10-heptachlorobornane (B7-1001, Hp-Sed) and 2-*endo*,3-*exo*,5-*endo*,6-*exo,*8,9,9,10-octachlorobornane (B8-1412) is described. Both compounds are components of toxaphene, an insecticide that has been widely used in the past. B7-1001 is an important toxaphene congener, comprising up to 99% of total toxaphene concentrations found in fish and sediment samples from treated lakes. B8-1412 is also a significant component of toxaphene contamination in samples from biota. In synthesizing the compounds, 2-*exo*,3-*endo*,6-*endo*,8,9,10-hexachlorobornane (B6-913) was obtained by reduction of the well-known toxaphene component P 32 (B7-515, 2,2,5-*endo*,6-*exo*,8,9,10-heptachlorobornane), which was itself isolated from the chlorination products of (+)-camphene. Chlorination of B6-913 provided B7-1001 in 49.5% yield, and P 32 and four other heptachlorobornanes were also detected in the reaction mixture. Structures of two of the heptachlorobornanes were elucidated by MS and NMR as 2-*exo*,3-*endo*,6-*endo*,8,9,9,10-heptachlorobornane (B7-1461) and 2-*exo*,3,3,6-*endo*,8,9,10-heptachlorobornane (B7-1303). B8-1412 was isolated from the product mixture obtained by chlorination of 2-*exo*,3-*endo*,6-*endo*,8,9,9,10-heptachlorobornane. Photolysis experiments at $\lambda = 254$ nm revealed that B6-913 is photochemicaly the most stable compound of the seven toxaphene compounds studied, with a $t_{1/2}$ of 213 h. B7-1001, having a $t_{1/2}$ of 82 h, was the second most stable compound. B8-1412 was degraded more rapidly, with a $t_{1/2}$ of 28.8 h, than B7-1001, but was still much more stable than P 50 (B9-1679, 2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-nonachlorobornane), which had a $t_{1/2}$ of 9.4 h, despite its reputation as a very persistant compound. Under the same experimental conditions hexachlorobenzene (HLB) and octachlorodibenzodioxine (OCDD) were consumed very quickly with $t_{1/2} = 0.0025$ and 0.0015 h, respectively.

**KEYWORDS: Toxaphene; single compounds; B6-923; B7-1001; B8-1412; photostability**

## INTRODUCTION

Toxaphene belongs to a class of widespread organochlorine contaminants that give rise to general concerns due to their ability to accumulate in the food chain and, thereby, pose potential risks even to humans (*1*−*3*). It is a complex mixture consisting of more than 1000 polychlorobornanes and polychlorocamphenes (*4*). In the United States, Canada, and western European countries, it has been banned since the early 1980s because of its toxicity, its environmental persistence, and its high potential for bioaccumulation (*5*). However, due to its relatively long half-life, it persists in the environment. The presence of these compounds is of great concern in the Canadian Arctic food web, in Great Lakes fish, and on the Canadian east coast (*6*−*9*). Atmospheric transport of toxaphene from cotton-growing regions in the southern United States has been considered as the major contamination source to these areas (*10*−*13*). Toxaphene was the contaminant responsible, at least in part, for the issuance of a total of six fish consumption advisories by four states of the United States (Arizona, Georgia, Oklahoma, and Texas) in 1998 (*1*).

An examination of sediment cores from two toxaphene-treated lakes in Canada showed that toxaphene peak pattern and concentration differed depending on sediment depth (*14*). The peak patterns of sediments from the years of treatment were similar to that of the technical toxaphene standard, whereas the peak patterns of the near-surface sediments were very different due to the absence of octa- and nonachlorobornane peaks in the chromatograms. Rainbow trout samples from both lakes showed a similar altered peak pattern. The most abundant hexachlorobornane is labeled Hx-Sed (B6-923, 2-*exo*,3-*endo*,6-*exo*,8,9,10-hexachlorobornane) and the most abundant heptachlorobornane, Hp-Sed (B7-1001) (*15*). B7-1001 constituted up to 99% of the total toxaphene concentration in sediment and

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fish samples from the treated lakes (*16*). B6-923 and B7-1001 were the most abundant toxaphene components in the sediment and biota samples from an estuarine salt marsh near a former toxaphene plant in Georgia (*17*). In air samples, which were found to contain transformed toxaphene residues, both B7-1001 and B8-1412 were detected (*18*, *19*).

In well-aerated soils, toxaphene is extremely persistent due to its highly oxidized nature. However, rapid degradation can take place in anaerobic soil environments (*20*). The main reaction under these conditions is reductive dechlorination, resulting in the formation of B6-923 and B7-1001 as major products (*21*). Studies on the degradation of single toxaphene components under anaerobic conditions confirmed the dependence of microbial dechlorination rates on the chlorine substitution pattern of the six-membered ring (*21*−*23*). B7-1001 has been identified as the main metabolite during anaerobic degradation of the toxaphene components having only a single chlorine atom at each secondary ring carbon atom in alternating orientation and chlorine atoms at carbon positions 8, 9, and 10. On the other hand, P 32 and five analogous compounds possessing 2,2,5-endo,6-exo chlorine substitution at the six-membered ring formed B6-923 and B6-913 upon degradation, which were stable metabolites (*24*). There is no information about the photostability of B7-1001 and B8-1412, whereas some data are available for several other toxaphene components (*21*−*23*, *25*−*28*).

Only stable components can be bioaccumulated and are therefore of toxicological relevance at the subacute or chronic level of exposure. Although some data exist on the toxicity of B6-923 (*29*), to our knowledge, there have been no toxicological studies on B7-1001 and B8-1412, primarily due to the lack of availability of these compounds in sufficient amounts. For the same reason, there is only very litle information about the environmental occurrence of B7-1001 and B8-1412. B7-1001 has been isolated in very small amounts from a toxaphene-like mixture and is available only in microgram amounts for analytical purposes (*30*). One aim of this study is therefore to develop a synthesis pathway for both compounds from P 32, which can be isolated in gram quantities from the technical mixture (*26*). Additionally, the photostabilities of toxaphene and seven single toxaphene congeners were studied in the presence of UV light and compared with those of hexachlorobenzene and octachlorodibenzodioxine.

## EXPERIMENTAL PROCEDURES

**General Procedures.** All chemicals were purchased from commercial sources and used without additional purification. If known, Parlar names (*31*) or AV codes (*32*) were used as trivial names for the chlorobornanes. The GC-MS measurements were performed with a mass selective detector (MSD, Hewlett-Packard 5970). The capillary column used was a 30 m × 0.25 mm × 0.25 $\mu$m DB-5MS column. Helium was the carrier gas with a flow of ~0.8 mL/min. A gas chromatograph equipped with an electron capture detector (ECD) was also used in some analyses. For GC-ECD analyses a DB-5 column was used, with a length of 60 m, i.d. of 0.25 mm, and film thickness of 0.25 $\mu$m. Nitrogen was used as the carrier gas with a flow of ~0.6 mL/min.

**$^{1}$H and $^{13}$C NMR Spectroscopy.** A Bruker AC-400 spectrometer was employed with tetramethylsilane (TMS) as a standard and deuterated chloroform ($CDCl_3$) as the solvent, but B7-1001 was measured in deuterated benzene ($C_6D_6$). An additional $^{13}$C NMR spectrum of B7-1001 was recorded in $CDCl_3$ with a 250 MHz instrument from Bruker. All chemical shifts were referenced to the solvent peak and recalculated with respect to TMS, $\delta$ ($^{1}$H) 7.24 ppm for $CHCl_3$.

**Synthesis.** *Step 1: Isolation of P 32.* P 32 was synthesized after modifying a previously published procedure (*26*). A magnetically stirred solution of 35 g of (+)-camphene in 300 mL of $CCl_4$ was chlorinated at 0 °C. The chlorination was first performed in the dark. After the camphene peak was observed to disappear by gas chromatography, the reaction was continued under a sun lamp and monitored by GC-MS. When a maximum concentration for P 32 was reached, the reaction was ceased. A 25 g portion of the product obtained, which contained P 32 at ~10%, was separated by column chromatography. The column (150 cm × 5.6 cm) was packed with silica gel (0.063−0.2 mm) and eluted with *n*-pentane. Elution of P 32 began after ~33 L of *n*-pentane had been eluted and was essentially complete after an additional 8 L of *n*-pentane. This procedure was repeated for a further three portions, each of 25 g. From the cyrstals obtained by concentration of the fractions, 1100 mg of P 32 was isolated in a purity of 99% after recrystallization from *n*-hexane. The yield was 1.1%.

*Step 2: Dechlorination of P 32 by Reduced Hematin To Obtain B6-913.* The reaction was performed as described by Saleh and Casida with little modifications (*26*). Briefly, 1050 mg of P 32 was treated with reduced hematin. From nearly 840 mg of crude product, which was purified with *n*-pentane on a silica gel column (100 cm × 3.0 cm), 90 mg of B6-913 was obtained in pure form, in addition to 440 mg of B6-923, 152 mg of 2,5-*endo*,8,9,10-pentachlorotricyclene, and 47 mg of 2,5-*endo*,6-*exo*,8,9,10-hexachlorobornene-2.

*Step 3: Chlorination of B6-913 and Isolation of B7-1001.* A solution of 90 mg of B6-913 in 100 mL of $CCl_4$ was chlorinated at 0 °C under a sun lamp. The reaction was monitored by GC-MS. To avoid overchlorination, the reaction was terminated after consumption of approximately half of B6-913. The chlorination product was chromatographed on a silica gel column (100 cm × 1.4 cm) to isolate the remaining B6-913, which was chlorinated again as described above to increase the B7-1001 yield. The purification of B7-1001 was performed by using a silica gel column (100 cm × 1.4 cm). *n*-Pentane was used as the elution solvent. Twenty-seven milligrams of B7-1001 could be obtained this way, in a purity of ~93%. Fourteen milligrams of 2-*exo*,3-*endo*,6-*endo*,8,9,9,10-heptachlorobornane (**4**, purity ~70%) and 2 mg of 2-*exo*,3,3,6-*endo*,8,9,10-heptachlorobornane (**5**, purity ~65%) were isolated as byproducts.

*Step 4: Formation of B8-1412.* This compound was obtained starting from **4** according to the same procedure used to obtain B7-1001. Thirteen milligrams of **4** was used for the chlorination. B8-1412 (2.4 mg) was isolated in a purity of 91% after silica gel chromatography using a column of 100 cm × 1.4 cm and pentane as elution solvent.

**Photolysis.** An oxygen-free solution containing 10 mg of toxaphene in 80 mL of *n*-hexane was irradiated with a high-pressure mercury lamp (HPK 125 W, Philips) jacketed with a water-cooled quartz filter ($\lambda \geq$ 230 nm) for 48 h. Samples were analyzed in 4 h intervals using GC-ECD. Photolysis of single compounds dissolved in cyclohexane was carried out in triplicate in quartz tubes (i.d. = 5 mm, length = 35 cm). Initial concentrations of individual compounds were 400 pg/$\mu$L. The solutions (5 mL) were purged of oxygen by passage through a gentle stream of nitrogen for 10 min before irradiation. Tubes were placed circularly at a distance of 2 cm around the light source (mercury low-pressure lamp, type Vycor 250 mA; Gräntzel, Germany) and irradiated at $\lambda_{max} = 254$ nm for up to 250 h. Sampling intervals varied widely and depended on degradation rates.

## RESULTS AND DISCUSSION

To obtain B7-1001 from B6-913 it was assumed that the introduction of the new chlorine should take place preferentially at the exo-position of the C-5 atom. The presence of an *endo*-chlorine at the neighboring C-atom should favor this reaction because of reduced steric hindrance. Product analysis confirmed this assumption; however, the yield was hampered by the formation of other heptachlorobornanes and further chlorination reactions (**Figures 1** and **2**).

Under the assumption that position 4 will not be chlorinated (*33*), eight different heptachlorobornanes are possible by substitution of a proton in B6-913. There can be only three different heptachlorobornanes, if the $CH_2Cl$ ($C_8$, $C_9$, and $C_{10}$) groups of B6-913 are chlorinated. The other five heptachlo-

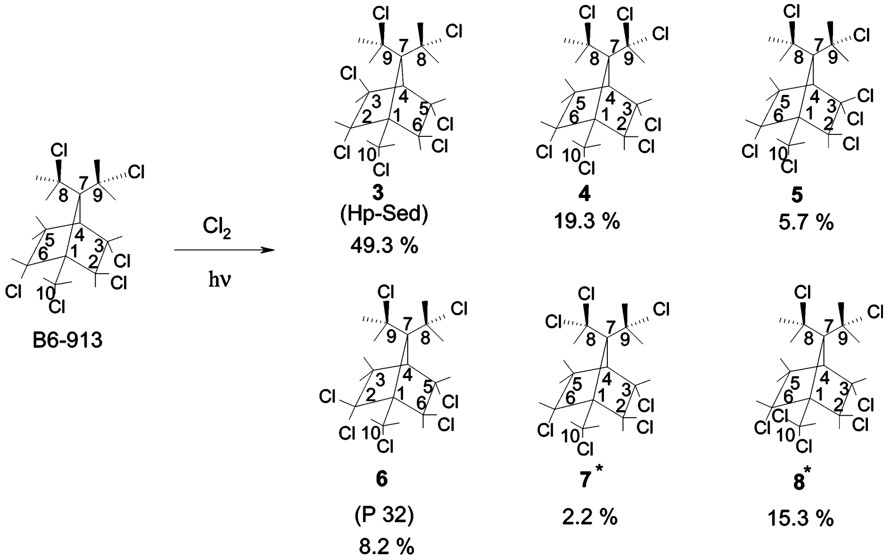

**Figure 1.** Formation of B7-1001 (**3**) and other heptachlorobornanes (**4**–**8**) from B6-913. The asterisks indicate unconfirmed structures.

robornanes can be formed by replacing one of the H atoms with chlorine at the 2-endo, 3-exo, 5-endo, 5-exo, and 6-exo positions. At least six different heptachlorobornanes were formed from B6-913 (**Figure 1**). The presence of the remaining two heptachlorobornanes in the reaction mixture cannot be excluded. However, no other heptachlorobornanes could be discerned with the DB 5 column used in this study. B7-1001 is by far the main product among the heptachlorobornanes, followed by compound **4** (**Figure 1**).

Compounds **7** and **8** could not be isolated. Fortunately, compound **8** showed the same relative retention time as 2-*exo*,3-*endo*,6-*endo*,8,9,10,10-heptachlorobornane (*34*). In that study, the retention order of chlorobornanes was given in dependence of chlorine substitution as 8,8,9,10 or 8,9,9,10 < 8,9,10,10, which was in agreement for compound **8**.

**Structure Elucidation by MS and NMR.** The number of $CH_2Cl$ and $CHCl_2$ groups in a chlorobornane molecule can be determined by studying the ratio of ion intensities of *m*/*z* 49 ($CH_2Cl^+$) to *m*/*z* 83 ($CHCl_2^+$) in an EI mass spectrum (*33*). If the ratio is >1, then there is no $CHCl_2$ group. The molecule possesses a $CHCl_2$ group if the ratio lies between 0.5 and 1. The ratios were 2.09, 2.10, and 2.32 for compounds **3**, **5**, and **6**, respectively. Compounds **4**, **7**, and **8** exhibited ratios of 0.74, 1.09, and 0.89, respectively. This indicates that compounds **4**, **7**, and **8** possess a dichloromethyl group, and the heptachlorobornanes **3**, **5**, and **6** should have four chlorines on the six-membered ring. Mass spectrometrical discrimination of these three compounds is rather complicated by the fact that the spectra are very similar. The number of chlorines at positions 8 and 9 cannot be determined by conventional EIMS (*33*). However, the mass spectrum of compound **8** differs from those of **4** and **7** by the presence of a significant peak group starting at *m*/*z* 327, which derives from the elimination of a $CH_2Cl$ group from $M^+$. Another ion in the mass spectrum of **8**, which does not exist in the spectra of **4** and **7**, is $[M - HCl - CH_2Cl]^+$, which is also present in the spectra of compounds **3**, **5**, and **6**. The agreement of the mass spectra of **4** and **7** indicates that both compounds should be structurally similar. Because of the lack of other useful fragment ions to identify **4**, **7**, and **8**, the mass spectra cannot be used to establish without a doubt which compound has two chlorines at $C_{10}$. Hence, the structure of **8** (B7-1462) is based on its relative retention time (*34*).

The mass spectrum of compound **3** is identical to that of B7-1001 (*15*), and no further comment is necessary. Instead, we focus our discussion on compound **5**. The structure of this substance cannot be deduced from its mass spectrum, but it can be assumed that the new chlorine is not added to the methylene group to produce 2-*endo*,3-*endo*,5-*endo*,6-*exo*,8,9,10-heptachlorobornane. The evidence for this assumption is that all heptachlorobornanes formed possess two peak groups starting at *m*/*z* 278 and 243, with the exception of B7-1001 and P 32, which have two chlorine atoms at each side of the six-membered ring. The first ion group corresponds to $[M - HCl - C_2H_3Cl]^+$, which is formed by a retro-Diels−Alder reaction after the cleavage of a HCl from the side of a six-membered ring with at least two chlorines at two adjacent carbons. This ion group is one of the major peaks. The latter ion group is probably formed from the first group at *m*/*z* 278 by cleavage of chlorine. HCl elimination is obviously favored from the side of the six-membered ring with two alternating chlorines. For instance, dehydrochlorination of P 32 in the presence of base yields 3,6,6,8,9,10-hexachlororobornene-2 and 2,5-*endo*,6-*exo*,8,9,10-hexachlorobornene-2 in a ratio of 2.4:1 (*35*). This behavior was explained by the greater acidity of the 5-*exo*-hydrogen compared with the 3-*exo*-hydrogen in P 32. From these considerations it may be deduced that compound **5** is either 2,2,3-*endo*,6-*endo*- or 2-*exo*,3,3,6-*endo*,8,9,10-heptachlorobornane.

Final confirmation of compound **3** as B7-1001 was made by comparison to known $^1H$ NMR data (*15*) (**Tables 1** and **2**). Additionally, we recorded a $^{13}C$ NMR spectrum, which is in agreement with the structure of B7-1001 (**Table 3**). The two quaternary carbon signals at $\delta$ 58.89 and 62.82 belonging to $C_1$ and $C_7$ cannot be assigned distinctly on the basis of our measurements (**Table 3**). This might be possible with heteronuclear multiple bond correlation (HMBC) experiments, but with bicyclic and similar compounds coupling constants do not follow the order $2J > 3J > 4J > 5J$ and are very strongly dependent on angle. Hence, HMBC is not very helpful. However, the proximal environment of the $C_1$ atom is equivalent in B7-1001, **4**, and **5**, whereas that of $C_7$ is equivalent only in B7-1001 and **5**. Chemical shifts of 62.3, 61.1, and 61.3 ppm are close and therefore designated to $C_1$ atoms of B7-1001, **4**, and **5**, respectively. On the other hand, the chemical shift of 64.3 ppm differs significantly from the other two values of 58.6 and 59.9 ppm, and consequently it can be assigned only to $C_7$ of compound **4** (**Table 3**).

The $^1H$ NMR spectrum of **4** differs from that of B7-1001 by the presence of a $CH_2$ group at 2.43 and 2.70 ppm on the carbon

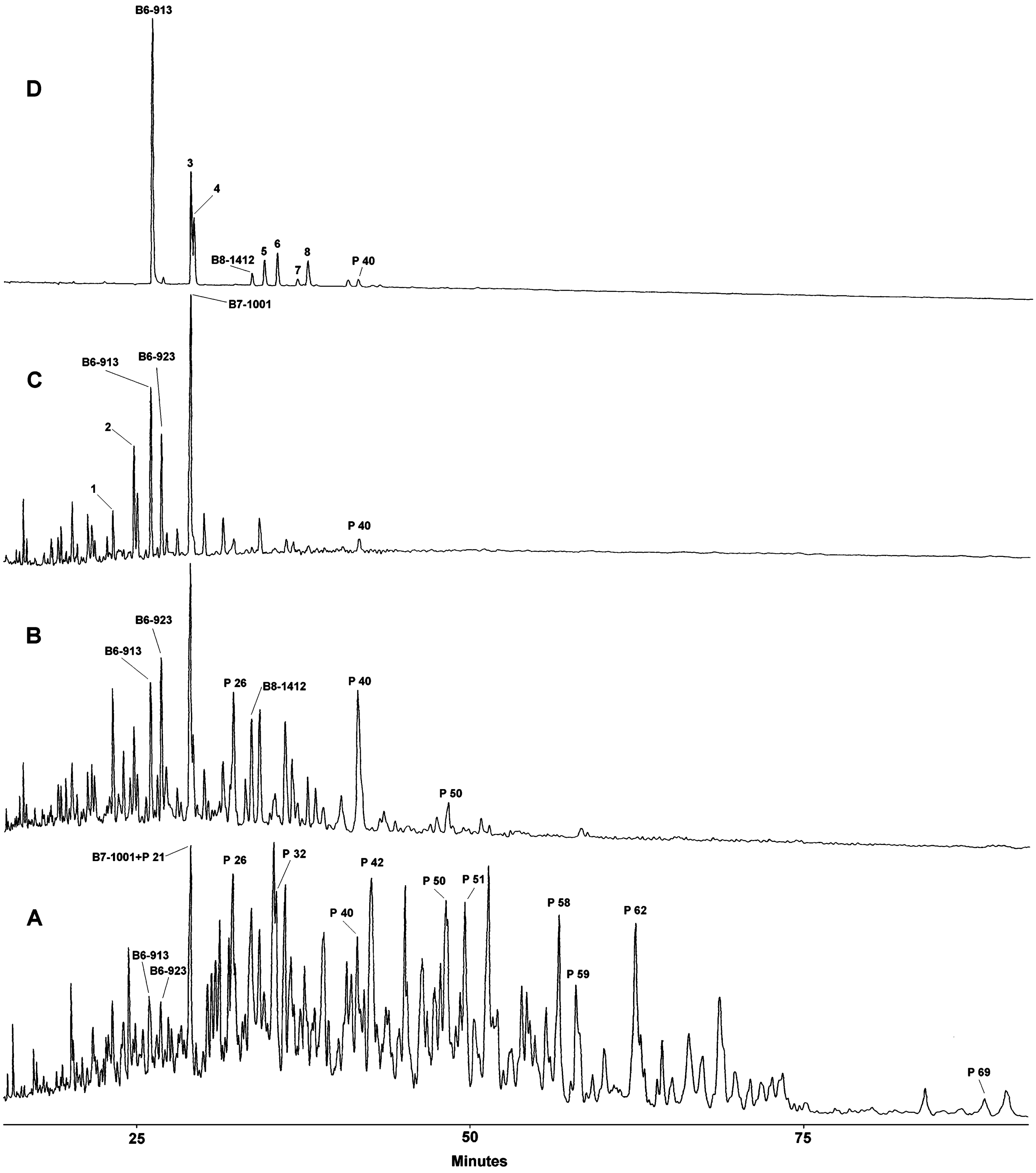

**Figure 2.** HRGC-ECD chromatograms of technical toxaphene (**A**), toxaphene irradiated for 12 h (**B**) and 48 h (**C**), and heptachlorobornanes (**3**–**8**) formed by chlorination of B6-913 (**D**).

**Table 1.** Proton Chemical Shift Data for **3** (B7-1001), **4**, and **5**[a]

| compd | $H_2$ | $H_3$ | $H_4$ | $H_{5-exo}$ | $H_{5-endo}$ | $H_6$ | $H_{8a}$ | $H_{8b}$ | $H_{8c}$ | $H_{9a}$ | $H_{9b}$ | $H_{9c}$ | $H_{10b}$ | $H_{10c}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** in $C_6D_6$ | 4.80 d | 4.58 d | 2.28 d | 3.82 t | | 4.38 d | 3.70 q | 3.48 d | | 3.98 q | | 4.39 d | 3.97 d | 3.12 d |
| **4** | 4.93 d | 4.60 o | 2.99 t | 2.70 m | 2.43 q | 5.01 q | 3.87 q | | 4.66 d | 6.88 d | | | 4.08 d | 3.57 d |
| **5** | 5.35 s | | 3.1 d | 2.75 o | 2.70 o | 4.99 q | 3.64 q | | 4.57 d | 4.9 q | 4.08 d | | 4.33 d | 3.58 d |

[a] Lettering of the positions at C8, C9, and C10 was made according to method of Hainzl et al., whereby 8a, 9a, and 10a mean downwards; 8b, 8c, in front of; and 8c, 9c behind the paper sheet; and 10a,10b, 10c counterclockwise (*33*). s = singlet, d = doublet, t = triplet, q = quartet, o = octet.

atom with 29.8 ppm, and a proton (6.88 ppm) exhibiting a long-range coupling of 1.9 Hz from a dichloromethyl group indicates that the introduction of chlorine must have occurred in either the $C_8$ or $C_9$ position. NOESY experiments lead to the conclusion that the dichloromethyl group is over $C_2-C_3$ and that compound **4** must be 2-*exo*,3-*endo*,6-*endo*,8b,9b,9c,10a-

**Table 2.** $^1$H NMR Coupling Constant Data for **3** (B7-1001), **4**, and **5**

| compd | $J_{23}$ | $J_{34}$ | $J_{35-exo}$ | $J_{45-exo}$ | $J_{5-endo/5-ex0}$ | $J_{5-endo/6-exo}$ | $J_{5-exo/6-endo}$ | $J_{5-exo/6-exo}$ | $J_{8ab}$ | $J_{8ac}$ | $J_{8a9a}$ | $J_{9ab}$ | $J_{9ac}$ | $J_{10bc}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** | 4.8 | | | 4.4 | | | 4.8 | | 12.2 | | 2.1 | | 12.1 | 12.6 |
| **4** | 4.8 | 4.5 | 2.1 | 4.7 | 15.3 | 4.8 | | 11.2 | | 13.7 | 1.9 | | | 12.8 |
| **5** | | | | 4.4 | 15.8 | 4.3 | | 10.5 | | 12.3 | 2.5 | 12.6 | | 12.5 |

**Table 3.** Carbon Chemical Shift Data for **3** (B7-1001), **4**, and **5**

| compd | C1 | C2 | C3 | C4 | C5 | C6 | C7 | C8 | C9 | C10 |
|---|---|---|---|---|---|---|---|---|---|---|
| **3** in $C_6D_6$ | 62.8 | 69.0 | 60.7 | 57.6 | 65.7 | 66.8 | 58.9 | 44.6 | 44.0 | 41.3 |
| **3** in $CDCl_3$ | 62.3 | 68.4 | 60.0 | 57.3 | 65.1 | 66.2 | 58.6 | 43.8 | 43.4 | 40.8 |
| **4** | 61.1 | 67.5 | 65.7 | 51.5 | 29.8 | 59 | 64.3 | 41.2 | 73 | 40.8 |
| **5** | 61.3 | 73.6 | 92.5 | 62.0 | 34.9 | 57.5 | 59.9 | 44.8 | 44.7 | 41.2 |

heptachlorobornane. This finding leads to the conjecture that compound **7** should be 2-*exo*,3-*endo*,6-*endo*,8,8,9,10-heptachlorobornane (B7-1458) because the positions of the other two dichloromethyl groups are already known. Compound **4** is identical to B7-1461, which was found as one of three primary degradation products of 2,2,5-*endo*,6-*exo*,8,8,9,10-octachlorobornane (B8-806) under anaerobic conditions (*36*).

It is apparent from the $^1$H NMR, $^{13}$C NMR, and $^1$H COSY spectra of compound **5** that there are three chloromethyl groups, one methylene group, and two chloromethylene groups. This means that there is a geminal dichloro group at the six-membered ring in either the $C_2$ or $C_3$ position. It is also evident from the $^1$H,$^1$H COSY spectrum that the protons at $\delta$ 4.99 ($C_6$) and 3.1 ($C_4$) are in the next neighborhood to the methylene protons at $\delta$ 2.75 and 2.70 ($C_5$). According to NOESY and HMQC spectra, the proton at 5.35 ppm does not couple with the $C_4$ proton at 3.1 ppm and also does not show any interactions with the proton at the $C_{9a}$ position, but with the $C_{10c}$ proton at 3.58 ppm. Consequently, the seventh chlorine must be located on the $C_3$ atom, and compound **5** must have the structure 2-*exo*,3,3,6-*endo*,8b,9c,10a-heptachlorobornane (B7-1303).

**Further Chlorination Reactions.** Chlorination of **4** and B7-1001 led to the formation of the octachlorobornane B8-1412 as the main product in nearly identical yields ( ~50%). MS and NMR data of B8-1412 from these reactions conform with those given in the literature (*37*). However, **4** was used as starting compound to prevent wasting B7-1001. Besides B8-1412, 2,2,5-*endo*,6-*exo*,8,8,9,10-octachlorobornane (P 42a, B8-806) was a major product, which has been considered in commercial analytical quantification standards together with 2,2,5-*endo*,6-*exo*,8,9,9,10-octachlorobornane (P 42b, B8-809) as one compound by suppliers, because up to now they could not be separated from each other (*38*). A third major product's structure was deduced from its mass spectrum as 2-*exo*,3-*endo*,6-*endo*,8,9,9,10,10-octachlorobornane (B8-1957). From B7-1001 five octachlorobornanes were formed. Apart from B8-1412, two of them were identified by comparison of retention times as 2,2,3-*exo*,5-*endo*,6-*exo*,8,9,10-octachlorobornane (P 39, B8-531) and 2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,9,10,10-octachlorobornane (P 40, B8-1414). This last compound was also the major chlorination product of a fraction containing compound **8** formed from B6-913. Chlorination of Hx-Sed yielded P 32 as the main product (>50%). 2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Octachlorobornane (P 50, B9-1679) was formed via chlorination from B8-1412 in high yield (>50%). These chlorination experiments revealed that suitable chlorobornanes can be used to obtain analytical standards of environmentally important toxaphene components.

**Photostability of Single Toxaphene Congeners.** Previous studies exhibit that photolysis of single toxaphene components gives only dechlorination or dehydrochlorination products, with reaction rates depending on the structure and chlorine number of parent compounds (*23*, *25*−*28*). Generally, during irradiation in solvents, the bornane structure is preserved (*39*).

The photolysis rate of studied compounds fits a first-order reaction kinetic profile with a half-life of

$$\ln(C_t/C_0) = -kt$$

$$t_{1/2} = \ln 2/k$$

where $C_0$ and $C_t$ are the concentrations at times 0 and $t$, respectively, and $k$ is the photolysis rate constant. The slope of a linear plot of $\ln(C_t/C_o)$ versus time gives the photolysis rate constant. Photolysis rate constants and half-lives are listed in **Table 4**.

In addition to the seven chlorobornanes, HCB and OCDD were irradiated for a comparison of degradation rates. Photostabilities of the studied compounds varied widely. From the chlorobornanes, P 32 was consumed most quickly, resulting in a $t_{1/2}$ of 3.9 h. B6-913 was the most stable chlorobornane, with a $t_{1/2}$ of 112 h, followed by B7-1001 and B6-923 with $t_{1/2}$ values of 82.0 and 76.5 h, respectively. **4** and B8-1412 were degraded more rapidly, having half-lives of 32.5 and 28.8 h, respectively, but these values were still significantly higher than that of P 50, with a half-life of 9.4 h. This is in agreement with previous studies, which counted P 50 as one of most stable toxaphene components (*22*, *23*). However, compounds B6-913, B6-923, B7-1001, **4**, and B8-1412 were not available at the time of those studies. B6-913's half-life was 74500 times longer than that of OCDD, which was degraded within a few seconds. HCB displayed a degradation rate comparable to that of OCDD. The extraordinary reactivity of HCB and OCDD is due to their high degree of chlorination and, unlike the chlorobornanes, their strong absorption of light at 254 nm because of their aromatic structures. It is to be noted that the half-lives given in this work are not relevant to environmental fate in water or the atmosphere except in a relative way.

**Structure and Photostability.** Some relationships are apparent between the photostability and structure of chlorobornanes (*22*, *23*, *25*). Introduction of a chlorine atom leading to a geminal group resulted in a higher degradation rate as a comparison of the half-lives of B6-913 (or B6-923) and P 32 shows. The position of the geminal group is also very important for photochemical degradation. For instance, P 32 has a geminal group at C-2 and was degraded 8.3 times more quickly than **4**, which has a dichloromethyl group at position 9. The presence of a second dichloromethyl group causes stability to drop noticably. P 50 and B8-1412 both have four chlorine atoms in alternating positions on the six-membered ring, which has been considered to be an important factor for stability (*22*, *23*). However, the $t_{1/2}$ of B8-1412 is 3 times longer than that of P 50, which has a second dichloromethyl group contrary to B8-1412, and this characteristic resulted in a much lower photostability. The number of chlorines also influences the degradation rate. For example, B7-1001 differs from B6-913 only by the presence of a fourth chlorine atom on the six-membered ring, and yet its half-life is 26.7% lower. In the same manner,

**Table 4.** Rate Constants and Half-Lives for the Decomposition of Studied Compounds in the Presence of UV Light ($\lambda$ = 254 nm)

| compd | B6-913 | B6-923 | B7-1001 | **4** | B8-1412 | P 50 | P 32 | HCB | OCDD |
|---|---|---|---|---|---|---|---|---|---|
| half-life $t_{1/2}$ (h) | 112 ± 8 | 76.5 ± 7 | 82 ± 12 | 32.5 ± 4 | 28.8 ± 3 | 9.4 ± 2 | 3.9 ± 0.5 | $(2.5 \pm 0.5) \times 10^{-3}$ | $(1.5 \pm 0.4) \times 10^{-3}$ |
| rate const $k$ ($h^{-1}$) | $(6.13 \pm 4.5) \times 10^{-3}$ | $9.05 \times 10^{-3}$ | $8.45 \times 10^{-3}$ | $2.12 \times 10^{-2}$ | $2.40 \times 10^{-2}$ | $7.37 \times 10^{-2}$ | 0.18 | 277.2 | 462 |
| rel rate const[a] | 1 | 1.5 | 1.4 | 3.5 | 3.9 | 11.9 | 28.7 | 45000 | 74500 |

[a] Values are rounded.

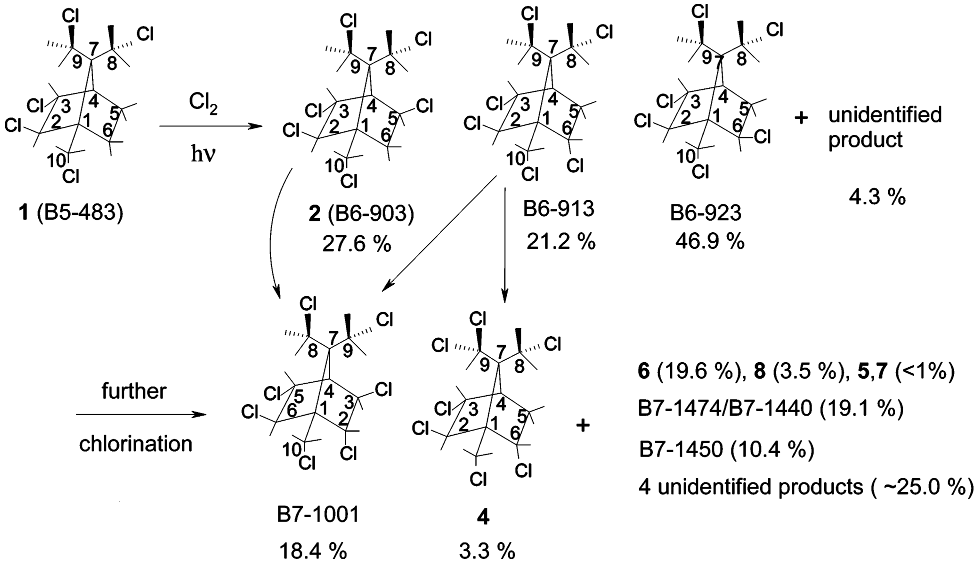

**Figure 3.** Chlorination products of 2-*exo*,3-*endo*,8,9,10-pentachlorobornane.

the $t_{1/2}$ values of **4** and B8-1412 differ, but only by 11.5% from each other. The reason for this relatively small difference is probably the presence of a dichloromethyl group in both compounds, which has a greater effect on the photostability than a fourth chlorine atom on the six-membered ring.

**Photoproducts.** When P 32 was photolyzed, 2,5-*endo*,6-*exo*,8,9,10-hexachlorobornene-2 was initially formed as the main product with B6-913 forming in similar concentrations and B6-923 forming in much lower amounts. However, further irradiation led to decomposition of 2,5-*endo*,6-*exo*,8,9,10-hexachlorobornene-2. In former studies of P 32 this bornene was not detected as a product (*26*). In our experiments, as long as P 32 was not completely degraded this compound was present in the reaction solution. From P 50 five compounds were formed but in very small amounts, together comprising ~4−6% of the starting concentration of P 50. Two of them could be identified as B6-913 and P 40 by matching their retention times to those of standards. No products could be detected by GC-ECD after photolysis of all other chlorobornanes, even if the compounds were photolyzed until total degradation.

**Photolysis of Toxaphene.** It has been shown that irradiation of toxaphene solutions causes slight degradation at wavelengths above 290 nm, but significant decomposition at wavelengths below 290 nm (*39*). On the other hand, irradiation of toxaphene adsorbed to silica gel at wavelengths above 290 nm resulted in mineralization to HCl and $CO_2$ (*27*, *28*, *40*). In previous work, toxaphene was photolyzed at 254 nm for 2 h, resulting in a mixture having a peak pattern which resembled that of toxaphene residues in many fish and cod liver oil samples (*41*).

Photolysis of toxaphene with UV light ($\lambda \geq$ 230 nm) initially led to rapid degradation of particularly highly chlorinated bornanes, which was in agreement with previous results (*41*) (**Figure 2**). After 12 h of irradiation, this mixture contained compounds such as B7-1001, P 26 (B8-1413), B8-1412, and P 40 as major components. These compounds are also especially prevalent in samples of aquatic biota in the northern hemisphere (*42*). Despite the degradation of several nona- and decachlorobornanes, the composition of this mixture was still very complex. A number of new compounds were detected in the retention time range of the hexa- to octachlorobornanes. Nevertheless, after 48 h of irradiation, the degree of degradation was 99.8%, and the GC-ECD chromatogram became very simplified, containing B7-1001 as the main compound. Other major components were B6-923, B6-913, 2-*exo*,3-*endo*,8,9,10-pentachlorobornane (compound **1**, B5-483), and two unknown hexachlorobornanes. The pentachlorobornane **1** was also reported as an anaerobic transformation product of B6-923 and B7-1001 (*43*). It should be noted that the irradiation times employed in this work are much longer than those of previous studies. It has been shown that all toxaphene components were degraded and that there were great differences in the degradation rates of individual compounds.

From the discussion so far one might expect that the two new apparently highly photostable hexachlorobornanes possess no geminal chlorine groups and that chlorines at adjacent carbon atoms are in alternating positions. Consequently, altogether there can be six different hexachlorobornanes besides B6-913 or B6-923, making the assumption that there are three chloromethyl groups. One supposition is that these hexachlorobornanes have structures similar to B6-913 or B6-923, by the dissimilarity that the third chlorine atom on the six-membered ring is located on the $C_5$ atom with endo or exo stereochemistry, resulting in 2-*exo*,3-*endo*,5-*exo*,8,9,10- or 2-*exo*,3-*endo*,5-*endo*,8,9,10-hexachlorobornane. Another supposition is that the positions of chlorine atoms at $C_2$ and $C_3$, for example, 2-endo,3-exo instead of 2-exo,3-endo, are exchanged. In this case, there are four possibilities for the third chlorine atom, namely, the 5-endo, 5-exo, 6-endo, and 6-exo positions. To ascertain the structures of two new hexachlorobornanes, 2-*exo*,3-*endo*,8,9,10-pentachlorobornane (**1**, B5-483) was chlorinated (**Figure 3**). B6-923 and

B6-913 were formed in 46.9 and 21.2% yields, respectively. Additionally, two other hexachlorobornanes were detected in 27.6 and 4.3% yields, and the first one (compound **2**, **Figure 2**) was also one of the major components of the irradiated toxaphene (**Figure 2**). Extended chlorination of 2-*exo*,3-*endo*,8,9,-10-pentachlorobornane yields, besides P 32 as the major heptachlorobornane, B7-1001, compounds **4**−**7**, 2-*exo*,3-*endo*,5-*exo*,8,9,10,10-heptachlorobornane (B7-1450), 2-*exo*,3-*endo*,6-*exo*,8,9,10,10-heptachlorobornane (B7-1474), 2-*exo*,3-*endo*,5-*exo*,6-*exo*,8,9,10,10-heptachlorobornane (B7-1440), B7-1462, and some other unidentified compounds. In this reaction, B7-1001 was formed in a much higher yield than was possible alone from the amount of B6-913, indicating that there had to be a second hexachlorobornane in a significant amount that reacted to form B7-1001. A further indication that all B7-1001 was not formed from B6-913 was the ratio B7-1001/**4** of 2.55 if B6-913 was chlorinated. This ratio increased to 5.5 by chlorination of **1**. As a consequence, only the compound with 27.6% yield having the structure 2-*exo*,3-*endo*,5-*exo*,8,9,10-hexachlorobornane meets all requirements for the experimental results mentioned above. This compund was recently identified as the major anaerobic transformation product from B7-1001 (*43*).

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**Supporting Information Available:** Mass spectra of **3**, **4**, **5**, **7**, and **8**; $^{13}$C NMR spectra of **3**, **4**, and **5**; $^{1}$H NMR spectra of **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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