Photodegradation of Dienochlor [Bis(pentachloro-2,4-cyclopentadien-1-yl)] by Sunlight

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A thin film of dienochlor [1, bis(pentachloro-2,4-cyclopentadien-1-yl)] on glass is readily degraded upon exposure to sunlight (half-life <1 h). Although irradiation of 1 with sunlight produces mostly a plethora of unknown products, four photoproducts were identified. Addition of two internally generated chlorine atoms to 1 gave a tricyclic chlorocarbon (2, up to 10% yield) which previously had been identified as the major photochlorination product from 1. Three isomeric perchloro ketones, each resulting from a net addition of one oxygen atom, were major photoproducts from sunlight irradiation of 1 as a thin film on glass (up to 14% yield of combined isomers) and on plants (up to 11% yield). The photoproducts from 1 in sunlight are compared to previous studies using 1 as a substrate in photochlorination, photooxidation (chlorine sensitized), and oxidation (with NO_2) reactions.

Dienochlor [1, Pentac miticide, bis(pentachloro-2,4-cyclopentadien-1-yl)] has been used on ornamental plants for control of phytophagous mites since 1964 (Allen et al., 1964). Although 1 is known to be photolabile in sunlight, its photodegradation products are heretofore unreported. In this work we focus on the identification of several photoproducts from 1 produced by sunlight. Such identifications were rendered possible only by application of reversed-phase liquid chromatography for isolation and ^{13}C NMR for analysis.

The photochlorination of 1 was studied in 1955 (McBee et al., 1955), but the advent of more powerful physical methods for spectroscopic analysis (e.g., ^{13}C NMR) was essential for structural identification of the resultant chlorocarbons (Smith and West, 1970; Mark and Weil, 1971). Thus, the photochlorination products described by Mark and Weil (1971) (Figure 1) formed the basis for our assessment of the sunlight photoproducts from 1. More recently the formation of stable peroxides from 1 has been demonstrated by a chlorine-sensitized photooxidation (Gäb et al., 1982). The work reported herein for the interaction of 1 with sunlight both confirms some and modifies other previous reports on photochlorination and photooxidation.

EXPERIMENTAL SECTION

[U-^{14}C]Dienochlor was used as a marker to determine yields of photoproducts and was prepared by Pathfinder Laboratories, St. Louis, MO (43.5 mCi/mmol). Radioactivity was detected by liquid scintillation counting (Packard Model 2425 spectrometers).

Analytical reversed-phase liquid chromatography (LC) was performed with a Spectra-Physics 8000A instrument: Spheri 5 RP-18 column, 25 × 0.46 cm, Brownlee Laboratories; elution at 1.6 mL/min and 35 °C; Model 8310 ultraviolet (UV) detector at 254 nm. Preparative reversed-phase LC utilized a LiChroprep RP-8 column (25 × 0.8 cm, Knauer) with a flow rate of 5 mL/min. The following conditions were used for normal-phase LC: Haskel Model 28030 pump; Spectra-Physics Model 8200 UV detector at 254 nm; Zorbax SIL column, 25 × 0.46 cm, 5 µm; elution at 1.3 mL/min. The following solvent systems were used for LC analysis: SS 1 (MeCN-0.1% HOAc, 75:25), SS 2 (MeCN-0.1% HOAc, 60:40), and SS 3 (pentane-ether, 99.5:0.5, half water saturated). Thin-layer chromatography (TLC) was performed on silica gel GF (Analtech).

^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL FX90Q Fourier transform spectrometer and are expressed in parts per million from Me$_4$Si as the external standard in CD$_2$Cl$_2$. Infrared (IR) spectra

were recorded by a Perkin-Elmer Model 281 spectrophotometer and UV spectra were obtained with a Perkin-Elmer Model 555 instrument. UV spectral data for 1 have been published (Mark and Weil, 1971). Mass spectral analysis employed a Hewlett-Packard Model 5985 instrument in the electron impact (EI) mode at 70 eV or in the chemical ionization (CI) mode with CH$_4$.

Isolation of Photoproducts. [^{14}C]Dienochlor (1, 2.06 g, 0.22 µCi/mmol) was dissolved in CH$_2$Cl$_2$ (5 mL) and uniformly coated on the interior surfaces of eight 4-6-L Erlenmeyer flasks. This application rate corresponds to 149 µg/cm^2 with a film thickness of about 2 µm. The flasks were exposed to direct sunlight (through ~2-mm Pyrex) for 37 h (June 13-16, 1980). After this exposure, the flasks were rinsed with CHCl$_3$ and methanol to remove 1 and its photoproducts (94% applied ^{14}C).

The photolysate was fractionated by chromatography on silica gel 60 (2.5 × 25 cm column, 0.063-0.200 mm, E. Merck) eluted with hexane. Two major fractions were collected, the first (eluted with 24 mL) containing a mixture of 1 and 2 which comigrated on a single UV-active spot upon TLC in hexane (R_f = 0.65). Unreacted dienochlor and 2 were separable by analytical reversed-phase LC (SS 1, k' = 8.7 and 10.3, respectively).

A second, silica gel column fraction was obtained by eluting with an additional 228 mL of hexane. TLC (hexane) of this fraction gave a single UV-active spot which was separable into the three isomeric perchloro ketones (i.e., 6, 7, and 8) by analytical reversed-phase LC (SS 2, k' = 13.6, 14.7, and 15.7, respectively).

Individual photoproducts were purified by preparative, reversed-phase LC. In order to isolate 2 for spectral identification, 130 mg of the above mixture of 1 and 2 from the silica column chromatography was fractionated by LC (SS 1). Compound 2 has very limited solubility in organic solvents; however, by making repeated 5-mg loop injections of 2 dissolved in acetonitrile-acetone (400 µL), it was possible to acquire 21 mg of pure 2 which was recovered from the LC eluent by ether extraction followed by TLC. Likewise, the perchloro ketone fraction (180 mg) from column chromatography was separated into 6 (94 mg), 7 (30 mg), and 8 (27 mg) by repetitive 20-mg injections of the mixture in 200 µL of acetonitrile and LC elution with SS 2. After LC rechromatography of each separate perchloro ketone, pure samples of 6, 7, and 8 were obtained. The purity of photoproducts 2, 6, 7, and 8 was >92% based on analytical LC and vindicated by the absence of extraneous resonances upon ^{13}C NMR analysis.

Perchloro Ketone 6. Mass spectrum m/z (rel intensity), EI, 494 (3), 492 (6), 490 (6), 488 (5), 486 (2, M$^+$ for Cl = 35), 455 (10), 357 (19), 355 (18), 274 (78), 272 (100),
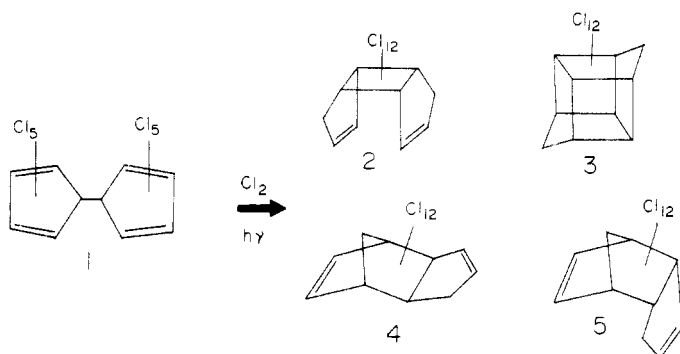
Zoecon Corporation, Palo Alto, California 94303.

Figure 1. Photochlorination products from dienochlor (1).

239 (58), 237 (95); IR (CCl₄) 1763 (s, C=O), 1613 (m, C=C), 1596 cm⁻¹ (m, C=C); UV (hexane) λ_{max} 268 nm (ε 2700), 243 (ε 7900).

Perchloro Ketone 7. Mass spectrum m/z (rel intensity), EI, 459 (0.7, M − Cl), 457 (1.3), 455 (1.9), 274 (77), 272 (98), 239 (59), 237 (100); IR (CCl₄) 1772 (s, C=O), 1607 (m, C=C), 1590 cm⁻¹ (m, C=C); UV (hexane) λ_{max} 235 nm (ε 13 000).

Perchloro Ketone 8. Mass spectrum m/z (rel intensity), EI, 451 (0.4, M − Cl), 274 (68), 272 (85), 237 (100), 235 (59); mass spectrum m/z (rel intensity), CI, 493 (8, M + H), 491 (12), 489 (6), 487 (2), 237 (19), 221 (47), 219 (100), 217 (78); IR (CCl₄) 1763 (s, C=O), 1607 (m, C=C), 1594 cm⁻¹ (m, C=C); UV (hexane) λ_{max} 234 nm (ε 9600).

Rate of Degradation of 1 on Glass. Dienochlor (2.9 mg, 0.15 mCi/mmol) was dissolved in acetone and uniformly coated on the interior, bottom surface (154 cm²) of 1-L Erlenmeyer flasks. After evaporation of the acetone, flasks were exposed to sunlight (July 10, 1980). At designated intervals (Figure 2) flasks were rinsed with CHCl₃ and MeOH to remove photoproducts which were analyzed by reversed-phase LC (SS 1 and SS 2).

Photodegradation of 1 on Plants. Immature cucumber and strawberry fruits were painted with an emulsion of [U-¹⁴C]dienochlor (20 µg/cm²). Plants were maintained in a greenhouse receiving direct sunlight. Periodically fruit were harvested and extracted with CHCl₃ and MeOH, and the extracts were analyzed by reversed-phase LC (SS 1 and SS 2).

Oxidation and Photochlorination. Dienochlor and various photoproducts were reacted with NO₂ according to Scribner (1965). The oxidation products were analyzed by normal-phase LC (SS 3) which separated the two perchlorodiones (9 and 10, $k' = 3.9$ and 4.1). Likewise 2, 8, and 9 (ca. 2 mg) each reacted with concentrated H₂SO₄ (200 µL) at 80 °C with magnetic stirring in a 1-mL conical vial, and the products were analyzed by normal-phase LC (SS 3).

The chlorine-sensitized photooxidation of 1 was repeated by using the method of Gäb et al. (1982). Dienochlor (0.5 g) was adsorbed on heat-activated silica (silica gel 60, Merck) and then irradiated with a 200-W mercury lamp (Hanovia). Products were analyzed by LC (SS 1 and SS 2).

RESULTS AND DISCUSSION

Dienochlor (1) is degraded rapidly by sunlight with a half-life of less than 1 h (Figure 2). Although most of the photolysate consisted of an intractable mixture of nondiscrete products, about 25% of the initial 1 was converted to nonpolar photoproducts which are the subject of this report. Thin-layer chromatography (TLC) of the photolysate revealed only two UV-active zones. The more nonpolar zone from preparative TLC was separated into
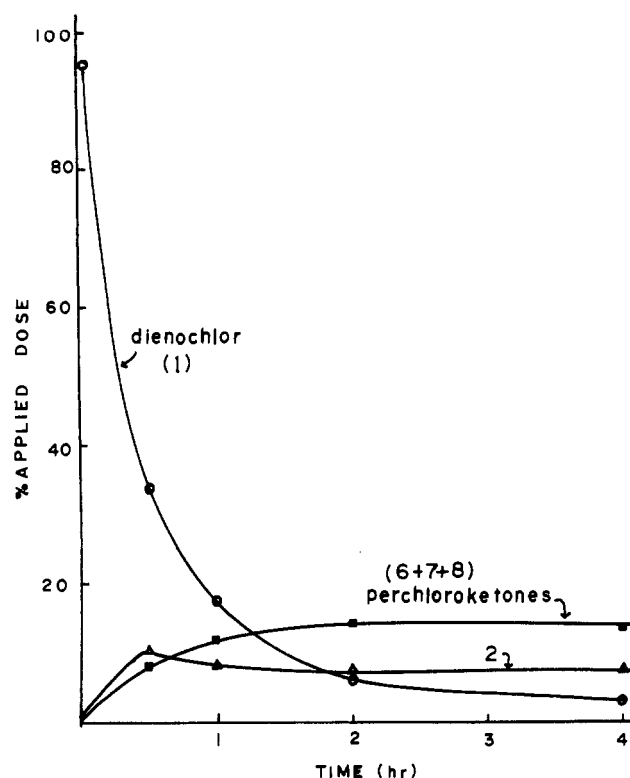

Figure 2. Photodegradation of dienochlor (1) as a thin film (19 µg/cm²) on glass.

2 and unreacted 1 by reversed-phase liquid chromatography (LC). Several additional minor components were also observed by LC of this fraction, but the known thermal rearrangement isomers of 1 were apparently absent (Smith and West, 1970; Mark and Weil, 1971).

Photoproduct 2 was purified by preparative LC for spectral analysis. The mass and infrared spectra of 2 were consistent with those published previously (Mark and Weil, 1971). Although previous workers were unable to obtain a ¹³C NMR spectrum of 2 because of its limited solubility (Mark and Weil, 1971), we obtained very satisfactory data by using a relaxation agent, Cr(acac)₃. The ¹³C chemical shift values were assigned readily (Table I) for 2 on comparison to numerous model chlorinated compounds of Hawkes et al. (1974), notably perchlorobicyclo[3.2.0]hept-2-ene. Compound 2 from sunlight photolysis of 1 exhibits identical spectral and chromatographic properties to 2 produced by the photochlorination of 1. Hence, since the ¹³C NMR spectrum clearly shows only five chemical shift resonances, the structure 2 originally proposed by Mark and Weil (1971) for the major photochlorination product from 1 is correct and an alternative structure proposed by other workers (McBee et al., 1955; Smith and West, 1970) is inconsistent with the ¹³C NMR data. The formation of 2 necessarily involves the net addition of two chlorine atoms to 1. Although we did not examine the mechanism of this reaction, these chlorines probably arise from the sp³ carbon(s) of a donor 1. A free radical mechanism such as that suggested by Smith and West (1970) may be involved.

The chemical reactivity of 2 produced by sunlight is also consistent with the assigned structure. Reaction of 2 with AlCl₃ under mild conditions (Gäb et al., 1982) gave 3 (mirex) in quantitative yield. Photoproduct 2 reacted with NO₂ at 100 °C (Scribner, 1965) to give similar amounts of two isomeric perchlorodiones (i.e., 9 and 10). Perchlorodione 9 was synthesized as a standard from reaction of 1 with NO₂ (Scribner, 1965) and its structure was as-

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Table I. ^{13}C NMR Spectral Data for Sunlight Photoproducts from 1

compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
2	76.2	83.2	76.2	83.2	140.3	131.8	92.3	92.3	131.8	140.3
7	76.0 or 75.3	74.4	75.3 or 76.0	78.1	157.2	138.2	183.1	91.2	132.0	139.5
8	73.8	70.6	78.9	83.4	159.3	137.6	181.6	90.7	132.3	139.0
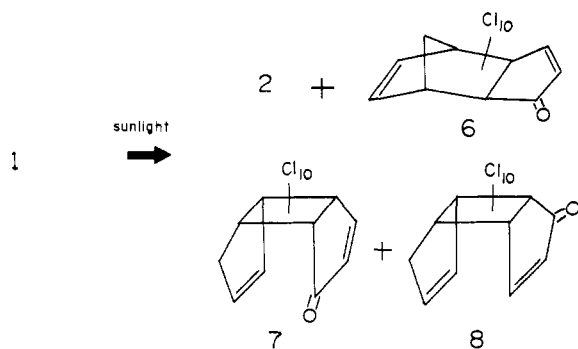
Figure 3. Photoproducts from dienochlor (1) exposed to sunlight.

Figure 4. Oxidation of sunlight photoproducts.

signed according to Padwa et al. (1971). Although previous workers (Scribner, 1965) have suggested tentatively the alternative, anti isomeric structure for the other perchlorodione (anti isomer of 10) arising from NO₂ reaction with 1, since 2 reacts with NO₂ to give the *same two perchlorodiones* as 1, we propose the syn structure (i.e., 10) for this second perchlorodione. Photoproduct 2 also is converted to 9 and 10 by concentrated H₂SO₄ at 80 °C.

Perchloro Ketones. Only one other UV-active, nonpolar photoproduct zone was observed on TLC analysis of the sunlight photolysate from 1. After isolation of this zone by preparative TLC, the initial analysis by LC using a mixture of methanol–0.1% acetic acid (80:20) suggested a single photoproduct. However, since mass spectral analysis suggested a single component with a molecular weight of 486 (1 + oxygen), but the ^{13}C NMR spectrum indicated three carbonyls, we immediately suspected the presence of a mixture of three isomers. Preparative LC with acetonitrile–0.1% acetic acid (60:40) separated this photoproduct mixture into its isomeric components. The LC isolation of these perchloro ketones was rendered particularly difficult by the limited solubility of each isomer in the LC eluent.

The most abundant perchloro ketone from sunlight irradiation of 1 (6, Figure 3) was identified readily from its ^{13}C NMR spectrum which almost perfectly matched a previously published spectrum (Hawkes et al., 1974). The mass spectral, ultraviolet, and infrared data also supported this structural assignment.

The two remaining perchloro ketones were identified only after careful consideration of alternative isomeric structures. The infrared spectra of both isomers indicated two different carbon–carbon double bonds in each compound and great structural similarity. The UV spectrum for each isomer was consistent with one conjugated, perchlorinated cyclopentenone ring. Since each perchloro ketone reacted with NO₂ (also H₂SO₄) to give in high yield approximately equal amounts of perchlorodiones (9 and 10, Figure 4), these perchloro ketones seemed to be analogues of 9 and 10 where one of the carbonyls in each case
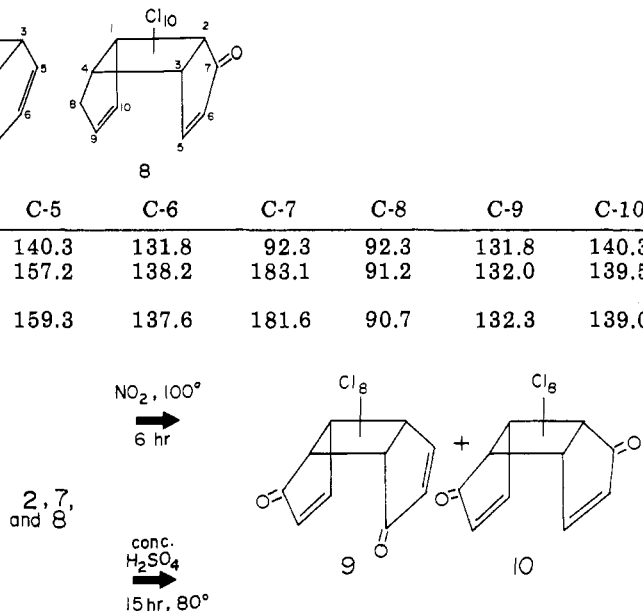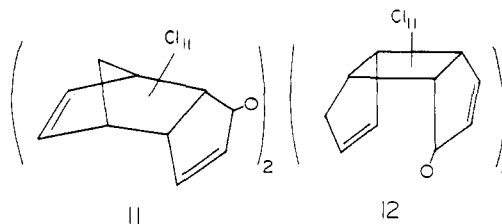
was replaced with a dichloromethylene moiety (Figure 3). This notion was reinforced by the isolation of these two perchloro ketones in low yield (high yield of perchlorodiones 9 and 10) from the reaction of 2 with NO₂, a finding which suggests a syn arrangement of the two five-membered rings about the cyclobutane ring.

The structural assignments of 7 and 8 to these perchloro ketones are based largely on the ^{13}C NMR spectra. In order to assign chemical shifts the ^{13}C NMR spectra of perchlorodione 9 (Padwa et al., 1971) and chlorocarbon 2 were used as models. When structures 7 and 8 were numbered as shown in Table I, the chemical shifts of analogous carbons can be compared directly. Hence, the largest difference in values occurs at C-4 which is the chloromethine carbon adjacent to the dichloromethylene. Since the chemical shift for C-4 of 8 (83.4 ppm) agrees best with the 2 model (83.2 ppm), the structures in Table I are assigned to 7 and 8 accordingly.

As mentioned previously, 2 reacts with NO₂ to give 7 and 8 if the reaction is quenched before complete formation of perchlorodiones 9 and 10. Since the ratio of 7 to 8 is 5:1, it appears that NO₂ reacts preferentially at C-5 (or C-10) of 2 [Table I; cf. Scribner (1965)]. However, once perchloro ketone 7 is formed, it seems to react with a second NO₂ nonregiospecifically since 9 and 10 are formed in similar amounts.

Peroxides from Chlorine-Photosensitized Oxidation of Dienochlor. With our results for comparison, we reexamined the work of Gäb et al. (1982), who alleged the formation of peroxide 11 as a photoproduct from the ir-

radiation of 1 on activated silica with a mercury lamp in the presence of chlorine and oxygen. Our structural assignments led us to doubt their proposed peroxide structure (i.e., 11), and this suspicion was enhanced since the

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Table II. Photoproducts from Dienochlor (1)

irradiation	dose rate, $\mu g/cm^2$	exposure time	% yield				
			1	2	6	7	8
sunlight							
thin film on glass	149	37 h	9.0	3.9	3.8	1.6	1.7
thin film on glass	19	4 h	3.0	7.8	9.0	4.1	0.7
strawberry fruit	20	7 days	30	<2	1.4	1.6	0.5
cucumber fruit	20	7 days	6	<1	0.9	0.8	0.6
mercury lamp	0.5/25[a]	4 h	31	17	4	6	2

[a] Grams per gram of silica.

reference (McBee et al., 1955) to rearrangement of 1 to a 3a,4,7,7a-tetrahydro-4,7-methanoindene on photochlorination was subsequently corrected by Mark and Weil (1971; i.e., 2 is the major product from photochlorination of 1, not the minor products 4 or 5). The peroxide zone (9% yield) was isolated by TLC and reduced with NaI to give perchloro ketones 6 and 7, and an unknown (1:5:1). The unknown perchloro ketone could well be the *endo*-perchloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one (i.e., endo isomer of 6) which would result from reduction of 11. However, since 7 is the major reduction product, this peroxide fraction is evidently a mixture containing predominantly the peroxide 12.

Environmental Photoproducts. The profile for the formation of photoproducts from 1 as a thin film on glass is shown in Figure 2. There is considerable similarity between the photochlorination and the sunlight photoproducts from 1 with 2 a major product in both cases. The formation of 2 by sunlight is particularly intriguing since it involves a net addition of two chlorine atoms. It is likely that 1 itself supplies these chlorines, i.e., a donor molecule of 1 may emit chlorine radicals upon irradiation as it is converted to a photolabile perchlorofulvalene. Although there is great structural similarity between 2 and mirex (3), a previous commercial insecticide, neither 2 nor 1 is converted to 3 by sunlight (<1% after 8 h).

The perchloro ketones are formed by at least two mechanisms. Since sunlight irradiation of 2 results in only traces of perchloro ketones, 2 itself is a poor direct progenitor of 7 and 8. However, 2 can be chemically oxidized by NO_2 to 7 and 8 so it is conceivable that these perchloro ketones arise partly from 2 reacting with oxidants in air. The perchloro ketones are formed also by conversion of 1 to relatively stable peroxides which slowly decompose to 6, 7, and 8. The corresponding perchlorodiones from 6, 7, and 8 are minor environmental photoproducts (<1%).

The photoproducts identified in this work from irradiation of 1 as a film on glass were less abundant when 1 was applied to plants and exposed to sunlight (Table II). Exposure of these plants (strawberry and cucumber fruit) to sunlight is a prerequisite for perchloro ketone formation by a nonmetabolic pathway. Although perchloro ketones 6, 7, and 8 were significant photoproducts on plants, the chlorocarbon 2 was undetectable. Dienochlor is relatively more stable in sunlight on plants than as a film on glass,

but the lability on glass is inversely proportional to the film thickness.

Thus, dienochlor (1) is considerably more photolabile than classical chlorinated hydrocarbons used for pest control. The identification of the photoproducts in this work was complicated by technical difficulties in isolation and analysis. For example, only reversed-phase liquid chromatography gave separation of the isomeric perchloro ketones, but preparative isolation was difficult because of the limited solubility of these compounds in the aqueous eluent. Since these chlorocarbons are devoid of hydrogen, ^{13}C NMR analysis was crucial for structure determination. However, the acquisition of relatively high (i.e., >5 mg) masses of pure product was essential for good spectral data since ^{13}C NMR analysis of these perchlorocarbons is substantially harder than most organic compounds because of the absence of Overhauser enhancement of ^{13}C signals associated with proton decoupling. Therefore, the isolation and identification of perchlorocarbons are still a challenging field.

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