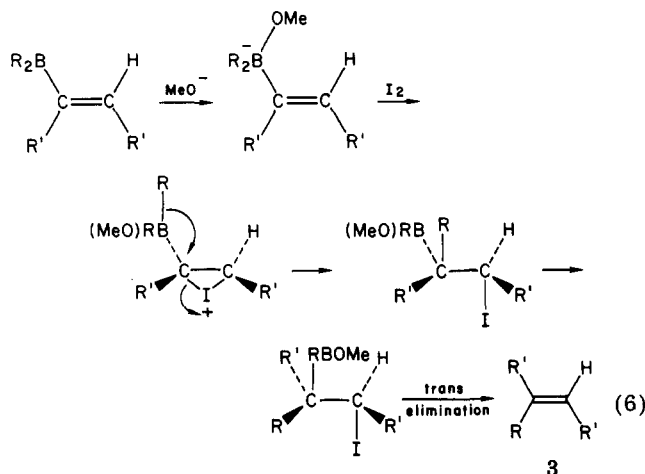


These results indicate that a mechanism analogous to that involved in the formation of cis disubstituted alkenes<sup>3a</sup> is operative. Apparently the reaction proceeds via trans addition, followed by trans elimination, resulting in the trans stereochemistry of the two alkyl groups from the internal alkyne (eq 6).



The following procedure for the synthesis of (3Z)-4-ethyl-3-dodecene is representative. To 8.16 g (30 mmol) of (*n*-C<sub>3</sub>H<sub>17</sub>)<sub>2</sub>BCl<sup>11</sup> were added 40 mL of THF and 3.4 mL of 3-hexyne (30 mmol) at 0 °C followed by a slow addition of LiAlH<sub>4</sub> in THF (7.5 mmol) with stirring. The reaction was allowed to proceed for 2.5 h at 0 °C, followed by 0.5 h at room temperature. Then the reaction flask was cooled to -78 °C and a solution of NaOMe in MeOH (120 mmol) and 7.7 g (30 mmol) of I<sub>2</sub> in 30 mL of THF were added, respectively, with vigorous stirring. After 3 h, the excess iodine was decolorized by adding an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and the reaction mixture was allowed to warm up to room temperature. The reaction mixture was extracted with 3 × 40 mL of pentane, and the organic layer was washed with 3 N NaOH solution (30 mL) and water and dried over anhydrous K<sub>2</sub>CO<sub>3</sub>. The solvents were removed under reduced pressure and distillation furnished 4.46 g (76%) of (3Z)-4-ethyl-3-dodecene bp 73-75 °C (0.6 mm), *n*<sub>D</sub><sup>20</sup> 1.4393. GC analysis showed >97% chemical purity.

For the assignment of stereochemistry, (2Z)-3-methyl-2-pentene was prepared from Et<sub>2</sub>BBr-SMe<sub>2</sub><sup>12</sup> and 2-butyne by following this procedure. The authentic samples<sup>10</sup> of (2Z)- and (2E)-3-methyl-2-pentene could be separated on a 12 ft × 0.25 in. column packed with 20% tricresyl phosphate on firebrick (60-80 mesh). The reaction product contained pure 2Z isomer (in 71% GC yield) as confirmed by coinjection with the authentic sample.

This reaction sequence represents a very convenient stereospecific synthesis of trisubstituted alkenes under mild conditions. We are presently exploring the possibilities of extending this procedure for the synthesis of more complex molecules.

**Registry No.** 2-Butyne, 503-17-3; 4-octyne, 1942-45-6; 5-decyne, 1942-46-7; 3-hexyne, 928-49-4; (z)-3-methyl-2-pentene, 922-62-3; (z)-2-cyclopentyl-2-butene, 79970-43-7; (z)-4-cyclopentyl-4-octene, 79970-44-8; (z)-5-cyclopentyl-5-decene, 79970-45-9; (z)-5-(2-butyl)-5-decene, 79970-46-0; (z)-4-ethyl-3-dodecene, 79970-47-1; (z)-3-methyl-2-nonene, 79970-48-2.

(11) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* 1979, 44, 2417.

(12) Prepared via the hydroboration of ethylene with BH<sub>2</sub>Br-SMe<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> [bp 70-72 °C (75 mm)].

(13) (a) Postdoctoral research associate on Grant GM 10937-19 from the National Institutes of Health. (b) Postdoctoral research associate, Purdue University.

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### Stable Peroxides from Chlorine-Photosensitized Oxidation of Perchlorinated Olefins

**Summary:** Chlorine-photosensitized oxidation of several perchlorinated olefins as neat liquids or adsorbed on silica gel leads to stable perchlorinated peroxides with α-chlorine atoms; these were identified by spectroscopic and X-ray crystallographic methods.

*Sir:* No perchlorinated peroxides with α-chlorine atoms appear to be described in the literature. Such compounds have been postulated as intermediates in order to explain the "aftereffect" sometimes observed in chlorine-photosensitized oxidations,<sup>1</sup> and indirect chemical<sup>1a</sup> evidence has been adduced for them. Highly-explosive α-chlorinated peroxides have been isolated from the reactions of ozone with 2,3-dichlorobutene<sup>2</sup> and of oxygen with vinylidene chloride,<sup>3</sup> but the product from reaction of oxygen with vinyl chloride is described as rather stable,<sup>4</sup> as are a series of α-chlorinated peroxides resulting from reaction of HCl with the corresponding α-hydroxy compounds.<sup>5</sup>

We have observed the formation of perchlorinated peroxides in the chlorine-sensitized oxidation of hexachlorocyclopentadiene (1), bis(pentachlorocyclopenta-2,4-dien-1-yl) (2), hexachlorobutadiene (3), tetrachloroethylene (4), and hexachloropropylene (5). The peroxide from 5 decomposes within 0.5 h at room temperature; the peroxides from 1-4, however, survive chromatography and are stable for many months at 5 °C.

The peroxides described here are most readily produced when the chlorinated olefins, adsorbed on silica gel under an atmosphere of oxygen and chlorine, are irradiated with visible light. While peroxides were also shown to result from irradiation of 1 and 3 as neat liquids, under these conditions the reaction is slower. Only trace amounts of peroxide resulted from irradiation of 1 in CCl<sub>4</sub> solution. We have not determined whether the higher rate in the adsorbed state is due to greater exposure of the chlorinated olefin to the chlorine and oxygen or to greater susceptibility of the double bonds to attack by chlorine radicals. It was shown for 1 and 3 that chlorine need not be present ini-

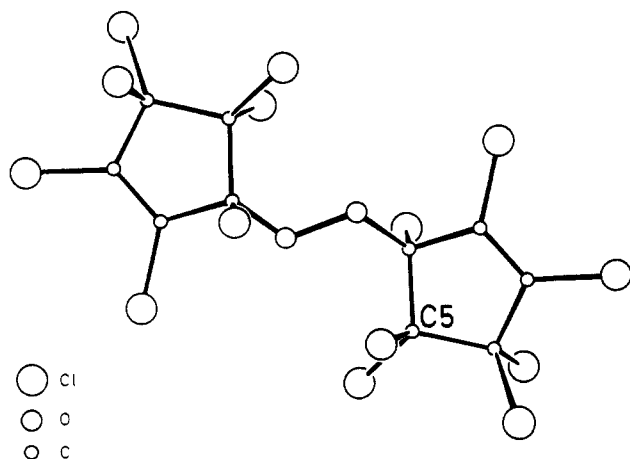
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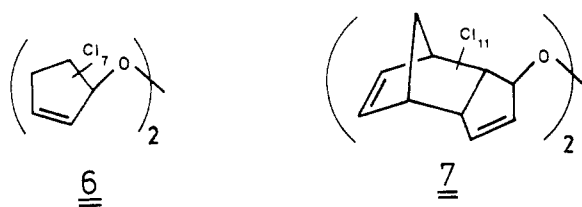
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**Figure 1.** Structure and solid-state conformation of 6.

tially; photolysis of these olefins with Pyrex-filtered UV light produces chlorine atoms for peroxide formation without significantly reduced yields.

In a typical experiment, 1 (4.0 g) and silica gel (200 g, previously dried for 24 h at 150 °C) were mixed for 24 h in a 4-L reactor flask.<sup>6</sup> The flask was evacuated and refilled to atmospheric pressure with oxygen. The mixture was irradiated with constant tumbling for 4 h with Pyrex-filtered UV light from a high-pressure mercury lamp (HPK 125 W, Philips). After extraction of the organics with  $\text{CH}_2\text{Cl}_2$  and removal of the solvent under vacuum, the oily residue (3.8 g) was chromatographed on silica gel with *n*-hexane to yield 0.88 g (22%) 1, 0.45 g (9.5%) peroxide 6,<sup>7</sup> 0.71 g (16.8%) hexachloro-3-cyclopentenone,<sup>8</sup> 0.30 g (7.1%) hexachloro-2-cyclopentenone,<sup>8</sup> and 0.06 g of 2<sup>9</sup> (1.7%). Similar percentage yields of peroxide result when as much as 40 g of 1 is irradiated, either neat or adsorbed on 200 g of silica gel.



The structure of the peroxide from 1 was established as 6 by single-crystal X-ray crystallography. The compound crystallizes from hexane in the triclinic space group  $P\bar{1}$  with cell dimensions  $a = 6.255 \text{ \AA}$ ,  $b = 8.413 \text{ \AA}$ ,  $c = 10.872 \text{ \AA}$ ,  $\alpha = 85.55^\circ$ ,  $\beta = 96.28^\circ$ ,  $\gamma = 113.4^\circ$ , and with one molecule in the crystal unit. The crystal structure was solved by direct methods, using MULTAN.<sup>10</sup> With anisotropic thermal parameters for all atoms 1017 nonzero reflections led to a value of  $R_1 = 0.045$ .<sup>11</sup> Figure 1 shows a computer-gen-

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(7) 6: mp 146–148 °C dec; IR (KBr) strong bands at 1605, 1195, 1090, 968, 765, 725, 710, 665  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR (20 MHz,  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$ )  $\delta$  137.65, 131.40 (vinyl), 106.25, 97.05 (probably  $\text{CClO}$  and homoallylic  $\text{CCl}_2$ , respectively), 92.95 (allylic  $\text{CCl}_2$ ); FD mass spectrum,  $m/e$  642 ( $\text{M}^+$ , based on  $^{36}\text{Cl}$ ); EI mass spectrum, (70 eV), base peak  $m/e$  251 ( $\text{C}_5\text{Cl}_6\text{O}$ ), highest observed mass  $m/e$  321 ( $\text{C}_5\text{Cl}_7\text{O}$ , relative intensity 0.7%); mol wt (vapor pressure in  $\text{CHCl}_3$ ), calcd for  $\text{C}_{10}\text{Cl}_{14}\text{O}_2$  648.4, found 663. Anal. Calcd C, 18.52; Cl, 76.54; O, 4.94. Found: C, 18.51; Cl, 76.40; O, 5.01.

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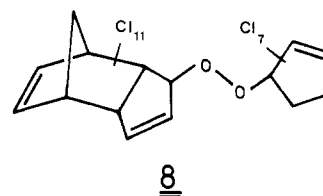
(10) Germain, G.; Main, P.; Woolfson, M. M.; *Acta Crystallogr., Sect. A* 1971, 27, 368.

(11)  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

erated structure of the molecule. The center of symmetry of the space group lies between the two oxygen atoms, lending the molecule  $C_i$  symmetry; the molecule is clearly the meso isomer. The bonds between carbon atom 5 and each of the neighboring carbon atoms are noticeably long (1.57 Å), probably as a result of Cl–Cl repulsions. The cyclopentane ring is in the envelope configuration, with carbon atom 5 deviating 0.51 Å from the plane of the other four carbon atoms.<sup>12</sup>

All these chlorinated peroxides can readily be detected in thin-layer chromatograms of crude mixtures and chromatography fractions by the immediate black spots they give when sprayed with diphenylamine; the other compounds become visible only very slowly or upon UV irradiation of the sprayed plates. TLC of the product mixture from 2 revealed two such peroxidic components, one of which was isolated as very insoluble crystals to which structure 7 has been assigned on the basis of spectroscopic and analytical data<sup>13</sup> and the product from reduction with iodide.<sup>14</sup> This peroxide was also shown to be a minor constituent of the reaction mixture from 1. As mentioned, small amounts of 2 are produced when Pyrex-filtered UV light is used in the preparation of 6. No 2 could be detected by GC when visible light with chlorine is used as initiator. 2 presumably arises by combination of pentachlorocyclopentadienyl radicals from UV photolysis of 1. The rearrangement of the carbon skeleton of 2 to that of 3a,4,7,7a-tetrahydro-4,7-methanoindene on attack by chlorine atoms is established.<sup>9</sup>

Another minor product obtained from 1 has been identified as the mixed peroxide 8,<sup>15</sup> which contains the elements of both 1 and 2. It can be prepared as the major peroxidic product, along with minor amounts of 6 and 7, by subjecting a mixture of 1 and 2 to the usual reaction conditions.



The peroxides obtained from 3 and 4 did not crystallize and have not been fully characterized. However, on the basis of  $^{13}\text{C}$  NMR spectra of the purest chromatographic fractions<sup>16</sup> and of their decomposition products, we have assigned them structures 9 (from 3) and 10 (from 4). Compound 10 is the compound proposed by earlier workers for the peroxidic product from gas-phase chlorine-photosensitized oxidation of 4.<sup>1d</sup> Compound 6 is analogous to 10 and apparently arises by the same mechanism; 9, though, must arise by intramolecular addition of the peroxy radical, followed by loss of a Cl atom. Indeed, the structure of 9 gives no clue to the main products of the

(12) A complete description of the structure, with all pertinent data, will be published in *Cryst. Struct. Comm.*

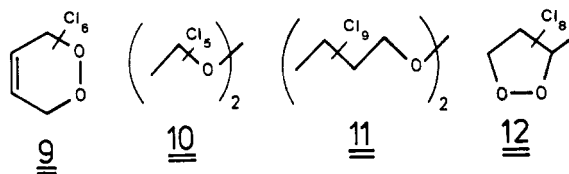
(13) 7: mp 168–171 °C; EI mass spectrum, base peak  $m/e$  270 ( $\text{C}_5\text{Cl}_6$ ), highest observed mass  $m/e$  521 ( $\text{C}_{10}\text{Cl}_{11}\text{O}$ , relative intensity 0.5%); IR (KBr) strong bands at 1596, 1205, 1180, 1130, 1025, 950, 898, 756, 723, 680, 633, 598  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{20}\text{Cl}_{22}\text{O}_2$ : C, 22.83; Cl, 74.13; O, 3.04. Found: C, 22.74; Cl, 74.50; O, 3.20.

(14) Reduction with iodide yields perchloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one.

(15) 8: mp 133–135 °C; IR (KBr) strong bands at 1600, 1190, 760, 725, 720, 680  $\text{cm}^{-1}$ ; EI mass spectrum, base peak  $m/e$  270 ( $\text{C}_5\text{Cl}_6$ ), highest observed mass  $m/e$  521 ( $\text{C}_{10}\text{Cl}_{11}\text{O}$ , relative intensity 0.4%); also supportive of 8 is an ion at  $m/e$  321 ( $\text{C}_5\text{Cl}_7\text{O}$ , 4%). Anal. Calcd for  $\text{C}_{15}\text{Cl}_{15}\text{O}_2$ : C, 21.18; Cl, 75.05; O, 3.76. Found: C, 21.36; Cl, 74.34; O, 3.70.

(16) 9:  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  131.50 (vinyl), 108.80 ( $\text{CCl}_2$ ). 10:  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  116.9 ( $\text{CCl}_2$ ), 99.7 ( $\text{CCl}_2$ ) at 10 °C.

oxidation reaction;<sup>17</sup> these appear, rather, to arise from peroxides such as 11 and 12, which we have not detected. The existence of a peroxidic component in the chlorine-sensitized oxidation of 5 is indicated only by the detection of a short-lived, nonpolar component giving the peroxide test with Ph<sub>2</sub>NH. The hazards of assigning a structure from the nature of the products are evident from the preceding example.



We are presently investigating further the product resulting when bromine, rather than chlorine, is used to sensitize the oxidation of 1. This is a bromine-containing peroxide which may be an analogue of 6.

Although no explosions or spontaneous decompositions were observed with these peroxides, care should be exercised in handling them. In view of their high chlorine content, they should also be assumed to be toxic.

**Registry No.** 1, 77-47-4; 2, 2227-17-0; 3, 87-68-3; 4, 127-18-4; 5, 1888-71-7; 6, 79991-54-1; 7, 79991-55-2; 8, 79991-56-3; 9, 79991-57-4; 10, 79991-58-5; hexachloro-3-cyclopentenone, 15743-12-1; hexachloro-2-cyclopentenone, 2514-52-5; perchloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one, 5263-60-5.

**Supplementary Material Available:** Table of atomic positional and thermal parameters for 6 and a structure showing the complete numbering scheme (2 pages). Ordering information is given on any current masthead page.

(17) These are perchloropropene and pentachloroacetone, believed to arise from 11 and 12, respectively.

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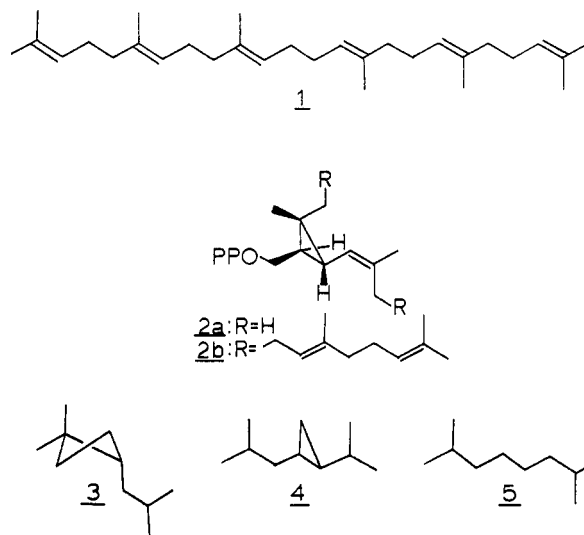
**Liborius Born**  
*Forschung und Entwicklung der Bayer AG*  
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 Received October 29, 1981

**trans-2-(2-Propenyl)-1-(2-methyl-1-propenyl)cyclopropane (Rothrockene). A Non-Head-to-Tail Monoterpenoid with a New Skeletal System from *Artemisia tridentata rothrockii*<sup>1</sup>**

**Summary:** The structure of *trans*-2-(2-propenyl)-1-(2-methyl-1-propenyl)cyclopropane (6), a monoterpene possessing a new non-head-to-tail carbon skeleton, has been determined by spectral and chemical means. The isolation of 6 supports the hypothetical analogy drawn between non-head-to-tail monoterpene biosynthesis and squalene biogenesis.

**Sir:** It has been proposed that non-head-to-tail monoterpene biosynthesis might serve as a model for the study of the biogenesis of the important triterpene squalene 1.<sup>2</sup> The formation of these non-head-to-tail terpenes presu-

ably involves ionization and rearrangement of the structurally analogous cyclopropyl intermediates, chrysanthemyl pyrophosphate 2a<sup>2</sup> and presqualene pyrophosphate 2b.<sup>3</sup> This hypothetical analogy predicts the occurrence of three irregular monoterpene skeletal systems 3, 4, and 5, in addition to those already known.



As part of this study we have been screening plants of the Anthemideae tribe of the Compositae family for irregular monoterpene components, and a number of new compounds have been identified.<sup>4-8</sup> We now report the isolation of a structurally novel compound obtained from the volatile oils of the sagebrush *Artemisia tridentata rothrockii* for which we propose the trivial name rothrockene and structure 6.

Essential oils of *A. tridentata rothrockii*<sup>9</sup> were obtained by techniques developed previously<sup>5</sup> and shown to contain a previously unidentified component. Isolation by silica gel chromatography, with final purification by preparative gas chromatography, afforded a fragrant oil which analyzed for C<sub>10</sub>H<sub>16</sub> (13.8% of oil): [α]<sub>D</sub> -64.8° (c, 1.33, CHCl<sub>3</sub>); IR (neat) 3060, 2950, 2900, 1635, 1450, 1440, 1410, 1375, 970, 885 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 0.61 (1 H, m), 0.95 (1 H, m), 1.32 (1 H, m), 1.52 (1 H, m), 1.67 (6 H, s), 1.72 (3 H, s), 4.62 (1 H, m), 4.67 (2 H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 13.8 (t), 18.3 (q), 19.2 (q), 20.8 (q), 25.6 (d), 27.1 (d), 108.0 (t), 127.5 (d), 131.2 (s), 145.7 (s); EI mass spectrum, *m/z* (relative intensity, %) 93 (100), 91 (40), 79 (33), 80 (32), 77 (27), 121 (22), 105 (18), 92 (18), 67 (13), 136 (8).

A consideration of the above data suggested the presence of isopropenyl [-C(CH<sub>3</sub>)=CH<sub>2</sub>] and isobutenyl [-CH=C(CH<sub>3</sub>)<sub>2</sub>] double bond moieties. A 1,2-disubstituted cyclopropyl ring system was indicated by the <sup>1</sup>H NMR chemical shifts and line patterns exhibited by the four protons at 0.61, 0.95, 1.32, and 1.52 ppm and by the fact that a ring is required to complete the three degrees of unsaturation dictated by the molecular formula. These units can be assembled to yield either a *cis*- or *trans*-dialkenylcyclopropane; however, the known thermal insta-

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(9) A voucher specimen, collected near Ephraim, UT, is available at the University of Utah Herbarium.

(1) Research supported by NIH Grants GM 20196 and GM 26245.  
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