

gel with chloroform-acetonitrile (70:30). This affords 0.66 mmol (0.170 g, 33%) of **2** and 0.76 mmol (0.185 g, 38%) of **18**. Additional treatment of **18** with an equivalent amount of  $\text{CH}_2\text{N}_2$  in dry ether affords quantitatively the product **2**: IR ( $\text{CHCl}_3$ ) 1705, 1620  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ , 360 MHz; for the spectral data of the C- and D-ring protons see Table I)  $\delta$  3.85 (s, 3 H, 2-OCH<sub>3</sub>), 4.00-4.50 (br s, 1 H, NH), 7.18-7.27 (m, 3 H, 1-H, 3-H, 4-H); mass spectrum,  $m/e$  (relative intensity) 258 (100), 243 (3), 230 (24), 216 (9), 215 (6); calcd for  $\text{M}^+$   $m/e$  258.1368, found  $m/e$  258.1368.

**6-Carboethoxy-6,7-diaza-2-methoxy-8-methylgibban-10-one** (**8**). Compound **2** (1 mmol, 0.258 g), 1 mmol (0.108 g) of  $\text{ClCOOEt}$ , and 1 mmol (0.101 g) of  $\text{NEt}_3$  are dissolved in 15 mL of dry  $\text{CH}_2\text{Cl}_2$ . The solution is stirred for 3 h at room temperature. The mixture is filtered, and the filtrate is evaporated in vacuo. The residue is purified by preparative TLC on silica gel with chloroform-acetonitrile (85/15), which affords 0.90 mmol (0.297 g) of **8**. Recrystallization from benzene-hexane gives white crystals: mp 149 °C; IR ( $\text{CHCl}_3$ ) 1725  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  1.35 (t, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.42 (d, 3 H, 8-CH<sub>3</sub>), 1.98 (dd, 1 H,  $J_{9A9B} = 12$  Hz,  $J_{9B8} = 7.2$  Hz, 9<sub>B</sub>-H), 2.12 (ddd, 1 H,  $J_{9A9B} = 12$  Hz,  $J_{9A8} = 7.5$  Hz,  $J_{9A11B} = 2.2$  Hz, 9<sub>A</sub>-H), 2.97 (t, 1 H,  $J_{5B5A} = 11.5$  Hz,  $J_{5B4b} = 11$  Hz, 5<sub>B</sub>-H), 2.97 (d, 1 H,  $J_{11A11B} = 12.5$  Hz, 11<sub>A</sub>-H), 3.10 (dt, 1 H,  $J_{11B11A} = 12.5$  Hz,  $J_{11B9A} = 2.2$  Hz,  $J_{11B8} = 1.3$  Hz, 11<sub>B</sub>-H), 3.30 (m, 1 H, 8-H), 3.32 (dd, 1 H,  $J_{4b5B} = 11$  Hz,  $J_{4b5A} = 7.6$  Hz, 4b-H), 3.72 (s, 3 H, 2-OCH<sub>3</sub>), 4.16 and 4.32 (ABX<sub>3</sub> pattern, 2 H,  $J_{AB} =$

11 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 4.51 (dd, 1 H,  $J_{5A5B} = 11.5$  Hz,  $J_{5A4b} = 7.6$  Hz, 5<sub>A</sub>-H), 7.2-7.5 (m, 3 H, 1-H, 3-H, 4-H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 20.1 MHz) 14.9 (OCH<sub>2</sub>CH<sub>3</sub>), 21.6 (8-CH<sub>3</sub>), 41.7 (5-CH<sub>2</sub>), 43.2 (9-CH<sub>2</sub>), 45.4 (4b-CH), 55.2 (11-CH<sub>2</sub>), 55.9 (2-OCH<sub>3</sub>), 58 (9a-C), 62.1 (OCH<sub>2</sub>CH<sub>3</sub>), 68.9 (8-CH), 105.8 (1-CH), 125 (3-CH), 126.4 (4-CH), 138.4 (4a-C), 145.6 (10a-C), 155.8 (6-NCO), 160.7 (2-C), 204 (10-CO); mass spectrum,  $m/e$  (relative intensity) 330 (63), 257 (10), 215 (22), 214 (24), 200 (100); calcd for  $\text{M}^+$   $m/e$  330.1579, found  $m/e$  330.1581.

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**Registry No.** **2**, 81097-50-9; **3**, 55288-51-2; **5a**, 81097-51-0; **5b**, 81097-52-1; **6**, 81097-53-2; **7a**, 81120-70-9; **7b**, 81097-54-3; **7c**, 81097-55-4; **7d**, 81097-56-5; **8**, 81097-57-6; **13-HCl**, 81120-71-0; **15a**, 81097-58-7; **15b**, 81097-59-8; **18**, 81097-60-1; di-*tert*-butyl azodicarboxylate, 870-50-8; diethyl azodicarboxylate, 1972-28-7; ethyl bromoacetate, 105-36-2; allyl bromide, 106-95-6; ethyl carbonochloridate, 541-41-3.

## Rearrangements in the Halogenation of Tetraalkylethylenes with *N*-Halosuccinimides and *tert*-Butyl Hypochlorite

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The reaction of *N*-halosuccinimides and *tert*-butyl hypochlorite with tetraalkylethylenes has been investigated. Halo-cation addition to the double bond occurs in a fast reaction, followed by abstraction of an allylic proton, resulting in a double bond shift. In tetraalkylethylenes lacking for structural reasons the possibility of a double bond shift, a homoallylic halogenation occurs to produce in the case of adamantylideneadamantane the 4(e)-halo derivative. The electrophilic halogenation of tetraalkylethylenes with *N*-halosuccinimides and *tert*-butyl hypochlorite is compared with the well-known radical-chain allylic halogenation of mono-, di-, and trialkylethylenes with these reagents and the reaction of chlorine with olefins. The halogenations described here are strongly reminiscent of the singlet oxygen ene reaction and the causes of this resemblance are discussed.

In this paper we describe the remarkable halogenation<sup>1,2</sup> of tetraalkylethylenes with *N*-halosuccinimides and *tert*-butyl hypochlorite. These reagents are well-known to give allylic halogenation in a radical-chain reaction.<sup>3</sup> We have found that with tetraalkylethylenes these reagents react cleanly in an ionic manner to give products that deviate in structure from the normally expected halogenation products of *N*-halosuccinimides and *tert*-butyl hypochlorite with mono-, di-, and trialkylethylenes. These conclusions were derived from the observations made during the halogenation of adamantylideneadamantane (**1**). We have found that **1** reacts with chlorine and benzene-sulfenyl chloride to give 4(e)-chloroadamantylideneadamantane (**2**) via an ionic pathway without any addition

to the double bond.<sup>4,5</sup> In an attempt to carry out radical chlorination, **1** was treated with 1 equiv of *N*-chlorosuccinimide (NCS) in boiling  $\text{CCl}_4$  containing a radical initiator. To our surprise the sole product was **2**. When this reaction was repeated in  $\text{CH}_2\text{Cl}_2$  in the absence of radical initiators at room temperature, a rapid (<5 min) reaction occurred and **2** was formed in quantitative yield. The reaction takes place also in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , or  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COOH}$  and the rate increases with increasing solvent polarity.<sup>6</sup> The same product **2** was obtained when

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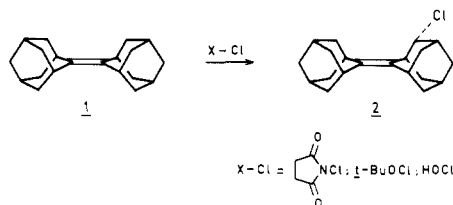


Figure 1.

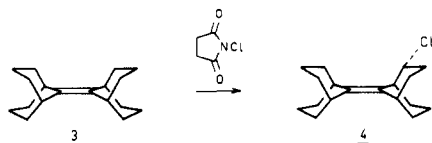


Figure 2.

*tert*-butyl hypochlorite (TBHC) or the combination NaOCl/CH<sub>3</sub>COOH was used as the chlorinating agent. When the reaction was performed in the presence of a radical inhibitor (hydroquinone), the same rapid conversion took place (Figure 1). With *N*-bromosuccinimide (NBS), a quantitative yield of 4(e)-bromo-adamantylideneadamantane was obtained, although heating for 12 h at 40 °C was necessary for complete reaction. When *N*-iodosuccinimide was employed, even in excess and under vigorous conditions, no reaction took place.<sup>7</sup>

A tetraalkylethylene closely related to 1 is bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (3).<sup>8</sup> In reaction with NCS, the 4(e)-chloro compound 4 could be isolated as sole product, whereas NBS does not react with 3 under the conditions used for 1 (Figure 2).

These stereoselective homoallylic halogenations are best explained by means of an ionic mechanism. The normal reaction of olefins with NCS, NBS, or TBHC affords halogenation at the allylic position; in 1 and 3 this reaction path is eliminated owing to steric hindrance. These results prompted us to investigate the reaction of these reagents with other tetraalkylethylenes. 2,3-Dimethyl-2-butene (5) reacts spontaneously and quantitatively with NCS and TBHC, forming 3-chloro-2,3-dimethyl-1-butene (6), free from detectable (by <sup>1</sup>H NMR) amounts of the thermodynamically more stable allylic isomer, 1-chloro-2,3-dimethyl-2-butene.<sup>9,10</sup> A tetraalkylethylene, offering both reaction types, namely, homoallylic chlorination and allylic chlorination with the double bond shift, is 2-adamantylideneadamantane (7).<sup>11</sup> The olefin 7 reacts similarly to 5 to furnish 8 in quantitative yield. The latter easily rearranges to 9, when passed through a SiO<sub>2</sub> column (Figure 3).

The structural result of this reaction, namely, introduction of a heteroatom accompanied by a shift of the double bond, is strongly reminiscent of the singlet oxygen (<sup>1</sup>O<sub>2</sub>) addition to olefins (ene reaction), as outlined for the transformation of 5 into 10.<sup>12</sup> A structural link between

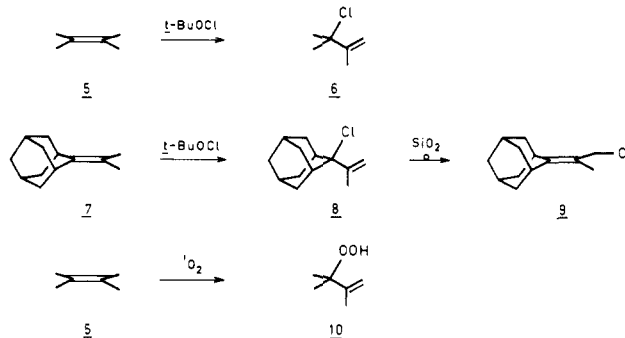


Figure 3.

the chlorinations reported here and the ene reaction of <sup>1</sup>O<sub>2</sub> was made with the syn olefin 11 and its anti isomer 12, which have been reported to form, in both cases, the two possible allylic hydroperoxides.<sup>13,14</sup> This result was offered as evidence against a concerted mechanism for the ene reaction of <sup>1</sup>O<sub>2</sub> with alkenes. We have examined the reaction of the same olefins with TBHC; when TBHC was used in C<sub>6</sub>D<sub>6</sub> solution, the only products observed were the allylic chlorides 13 and 14 in a ratio 2:1 as determined by <sup>1</sup>H NMR, starting from either 11 or 12. The allylic chlorides 13 and 14 are very sensitive to HCl elimination, yielding 4,4'-di-*tert*-butyl-1,1'-bicyclohexenyl (15, Figure 4).

### Discussion

The results presented here provide strong evidence for the ionic reaction of NCS, NBS, and TBHC with tetraalkylethylenes. All products are formed in a very rapid reaction in quantitative yield at room temperature without radical initiators. In contrast, when NCS, NBS, and TBHC are allowed to react with tri-, di-, or monoalkylethylenes, radical initiators (light or peroxides) are needed, resulting in halogenation at the allylic position to form usually the thermodynamically most stable product in excess.<sup>3</sup> An exception must be made for the reaction of these reagents in alcoholic solvents and Me<sub>2</sub>SO-H<sub>2</sub>O, in which addition to the double bond occurs in an electrophilic fashion.<sup>15</sup> Two halogenations with shift of the double bond are known in steroid chemistry, although this shift is favored by the formation of an  $\alpha,\beta$ -unsaturated ketone,<sup>16,17</sup> as is shown for the conversion of 16 into 17<sup>16</sup> (Figure 5).

Whether NCS, NBS, and TBHC react in a radical fashion with an olefin or via an ionic pathway appears to be governed by the electron density of the double bond in question. The radical-chain reaction of olefins with lower electron density at the double bond is well established.<sup>1,3</sup> However, when the olefins are electron rich—as is the case in tetraalkylethylenes and probably also with alkenes such as enol ethers—reagents such as TBHC, NBS, and NCS serve as halo-cation sources to form the halonium ion of the olefin with the base as counterion. The key

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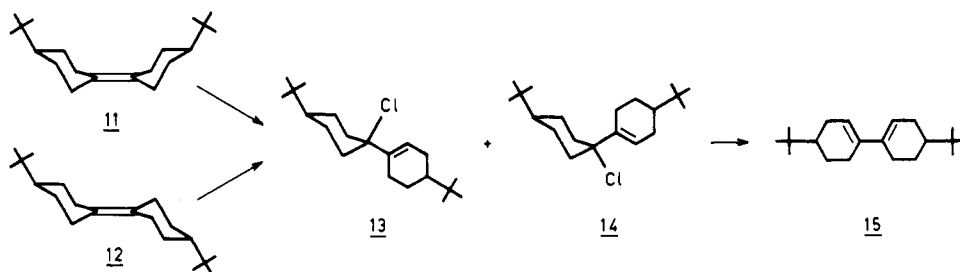


Figure 4.

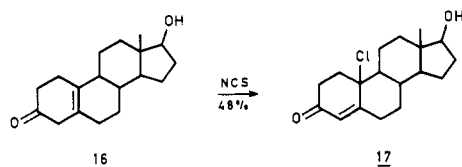


Figure 5.

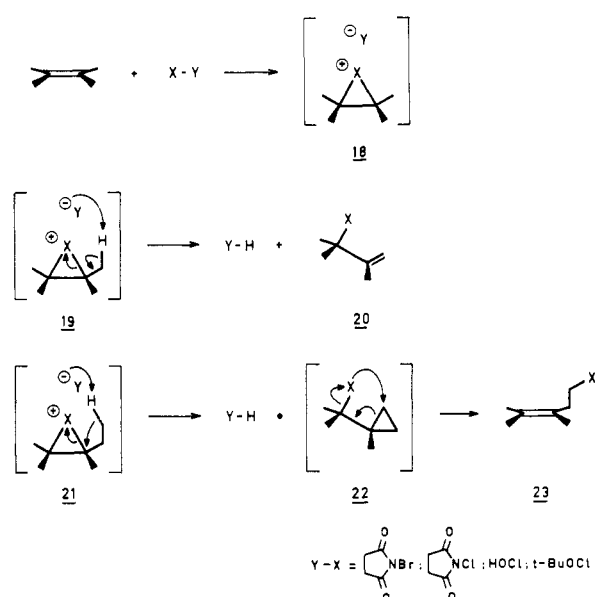


Figure 6.

intermediate 18 is shown here in a symmetrically bridged structure (Figure 6). The base, succinimide-, *tert*-butoxide-, or hydroxide-anion is capable of abstracting a proton. When an active allylic proton is present, as in 5, 7, 11, and 12, proton abstraction occurs at this position (see intermediate 19). The result is the formation of an allylic halide 20 in which the double bond is shifted relative to the starting olefin. This reaction is strongly reminiscent of the reaction of chlorine with olefins in the liquid state in which substitution competes with addition.<sup>18</sup> This substitution by chlorine in tetra- and trialkylethylenes is almost completely ionic; but for mono- and dialkylethylenes there is a competition between ionic and radical reactions.<sup>19</sup> Noteworthy is the high yield of 6 from 5 under these conditions.<sup>10</sup>

In tetraalkylethylenes 1 and 3 a double bond shift cannot occur. In these cases, therefore, a homoallylic proton is abstracted by the base (see intermediate 21), furnishing an  $\alpha$ -halocyclopropane 22. The latter rearranges easily to the stable 23, in which the halide occupies the equatorial

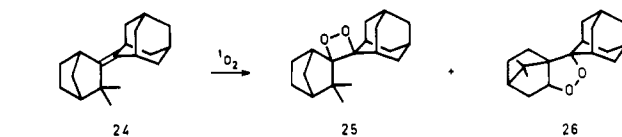


Figure 7.

position. Evidence for the electrophilic mechanism (see intermediates 21 and 22) is the formation of the bromonium ion of 1 when 1 and NBS are allowed to react in the presence of strong acids.<sup>20,21</sup> In addition, the major product in the bromination of norbornene in Me<sub>2</sub>SO with NBS is an  $\alpha$ -bromocyclopropane derivative.<sup>22</sup> The formation of a cyclopropane in the adamantane skeleton and the stereoselective addition to this dehydroadamantane have been reported previously.<sup>23</sup> Moreover the rearrangement of 22 into 23 probably takes place via a not completely free carbonium ion since otherwise acetate formation would have occurred in the presence of acetic acid as cosolvent.<sup>24</sup> Two other routes to 2 have been reported. The decomposition of the chloronium ion of 1 affords 2 in moderate yield.<sup>4</sup> This chlorination probably takes place via the same mechanism as described for NCS, TBHC, and HOCl and not via the Wagner–Meerwein type rearrangements published earlier.<sup>4,25</sup> Secondly, the interaction of benzenesulfonyl chloride with 1, furnishing 2 in high yield (85%), is explained on the basis of a dehydroadamantane intermediate.<sup>5</sup>

Noteworthy is the striking resemblance of these chlorinations to the singlet oxygen (<sup>1</sup>O<sub>2</sub>) additions.<sup>8</sup> The structural consequence—introduction of a heteroatom with shift of the double bond—is identical. Moreover the stereochemical aspects of the <sup>1</sup>O<sub>2</sub> ene reaction and the chlorinations described here are clearly related as outlined for the syn and anti olefins 11 and 12.<sup>10</sup> This similarity needs stressing in view of the “one of a kind” discussions often encountered in analysis of the mechanism of <sup>1</sup>O<sub>2</sub> reactions. Central in these discussions are often the peroxide or the open zwitterionic intermediates.<sup>26</sup> In halonium ion chemistry in which the structures could be studied by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy,<sup>27</sup> a bridged structure is pro-

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posed for a symmetrically substituted olefin (in terms of  $^1\text{O}_2$  chemistry: the perepoxide). An "open"  $\alpha$ -halo cation has been established for an unsymmetrically substituted olefin (in terms of  $^1\text{O}_2$  chemistry: the zwitterionic peroxide). The electronic properties of the substituents determine the extent of the bridging. In these terms an explanation can be found for the observation that only an open zwitterionic peroxide is quenched in the reaction of  $^1\text{O}_2$  with (silyl)enol ethers.<sup>28</sup> An analogy to the homoallylic halogenation may also exist in  $^1\text{O}_2$  chemistry, namely, in the remarkable rearrangement in the  $^1\text{O}_2$  addition to tetraalkylethylene 24 found by McCapra.<sup>29</sup> This rearrangement furnishes a dioxolane 26, which can be formed by a homoallylic proton abstraction followed by a cyclopropane ring opening (Figure 7). This suggestion does not preclude, of course, the earlier proposed mechanism via Wagner-Meerwein shifts.

In summary we emphasize that the present results provide additional support for the electrophilic character of the halogenation of tetraalkylethylenes with *N*-halosuccinimides on *tert*-butyl hypochlorite. These reactions furnish in high yield starting materials used subsequently in the synthesis of stable 1,2-dioxetanes.<sup>7,8</sup> The structural aspects of the rearrangement observed during this halogenation bear an obvious resemblance to the allylic rearrangement observed in the ene reactions of alkenes with singlet oxygen. This structural analogy hints at a corresponding mechanistic analogy.

### Experimental Section

**Instrumentation.** Melting points were determined on a Mettler FP2 melting point apparatus. IR spectra were recorded on a Unicam (SP-200) spectrophotometer.  $^1\text{H}$  NMR spectra were recorded at 60 MHz (Varian A-60 or Hitachi Perkin-Elmer R-24 B).  $^1\text{H}$  chemical shifts are reported in  $\delta$  units (parts per million) relative to  $\text{CHCl}_3$  and converted to  $\delta \text{Me}_4\text{Si}$  values, using  $\delta(\text{CHCl}_3) = 7.25$  ppm.  $^{13}\text{C}$  NMR spectra were recorded at 25 MHz (Varian XL-100) and  $^{13}\text{C}$  chemical shifts are denoted in  $\delta$  units (parts per million) relative to the solvent  $\text{CDCl}_3$  and converted to  $\delta \text{Me}_4\text{Si}$  values, using  $\delta(\text{CDCl}_3) = 76.9$  ppm. Mass spectra were recorded on an AEI MS-902 spectrometer. Elemental analyses were performed in the microanalytical section of this department.

**Solvents.** All solvents used were purified according to standard procedures.

**Chlorinating Agents.** The chlorination agents NCS, NBS, *N*-iodosuccinimide, and  $\text{NaOCl}/\text{CH}_3\text{COOH}$  were obtained commercially and used as such. TBHC was prepared according to a published procedure.<sup>30</sup>

**Tetraalkylethylenes.** The tetraalkylethylenes, adamantylideneadamantane (1),<sup>31</sup> bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (3),<sup>32</sup> 2-adamantylidenepropene (7),<sup>11</sup> *syn*- and *anti*-4,4'-di-*tert*-butylcyclohexylidene-cyclohexane (11 and 12)<sup>14</sup> were prepared by known procedures. In our hands 7 is a crystalline compound, mp 34–38 °C, instead of an oil. 2,3-Dimethylbut-2-ene (5) was obtained commercially and used without further purification.

**4(e)-Chloroadamantylideneadamantane.** To a solution of 1 mmol (268 mg) of adamantylideneadamantane in 20 mL of  $\text{CH}_2\text{Cl}_2$  was added 1.05 mmol (140 mg) of *N*-chlorosuccinimide. The reaction mixture was stirred for 1 h at room temperature, diluted with  $\text{CH}_2\text{Cl}_2$ , and washed twice with water. The organic

layer was dried over  $\text{MgSO}_4$  and evaporated. The yield of 4(e)-chloroadamantylideneadamantane was 300 mg (98%): mp 142–143 °C (lit.<sup>4,5</sup> mp 144–145 °C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.15 (br s, 1 H), 3.05 (br s, 1 H), 2.8 (br s, 3 H), 2.6–1.15 (br m, 22 H). When 0.1 mmol of hydroquinone is added to the solution, exactly the same reaction occurs and the product could be isolated in almost the same quantitative yield.

**4(e)-Bromoadamantylideneadamantane.** To a solution of 3 mmol (804 mg) of adamantylideneadamantane in 40 mL of  $\text{CH}_2\text{Cl}_2$  was added 6.6 mmol (1.175 g) of *N*-bromosuccinimide. The reaction mixture was refluxed and stirred for 12 h. The reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  and washed twice with water and a saturated  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The organic layer was dried over  $\text{MgSO}_4$  and evaporated. The yield of 4(e)-bromoadamantylideneadamantane was 1.05 g (97%). An analytically pure sample was obtained by crystallization from acetone and sublimation [115 °C (0.002 mm)]: mp 130.5–131.5 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.4 (br s, 1 H), 3.05 (br s, 1 H), 2.8 (br s, 3 H), 2.6–1.2 (br m, 22 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  136.9 (s), 131.0 (s), 63.8 (d), and 12 signals between 39.9 and 27.6; mass spectrum,  $m/e$  346:348 (1:1). Anal. Calcd: C, 69.16; H, 7.84; Br, 23.01. Found: C, 69.21; H, 7.82; Br, 22.99.

**4(e)-Chlorobicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane.** To a solution of 200 mg (0.82 mmol) of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane in 20 mL of  $\text{CH}_2\text{Cl}_2$  was added 115 mg (0.86 mmol) of *N*-chlorosuccinimide. The reaction mixture was refluxed and stirred for 1 h and  $\text{CH}_2\text{Cl}_2$  was added to dilute the reaction mixture. The organic layer was washed twice with water, dried over  $\text{MgSO}_4$ , and evaporated. The yield of 4(e)-chlorobicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane was 190 mg. Purification was done by chromatography (hexane,  $\text{Al}_2\text{O}_3$ ) and sublimation [45 °C (0.01 mm)]: mp 50–53 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.4–3.9 (m, 1 H), 2.85 (br s, 3 H), 2.5–1.2 (br, 22 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  136.8 (s), 129.7 (s), 66.0 (d), and 13 lines between 39.7 and 21.7; mass spectrum,  $m/e$  278:280 (3:1); exact mass calcd 278.180, found 278.182.

**Reaction of *N*-Chlorosuccinimide with 2-Adamantylidenepropene.** To a stirred solution of 208 mg (1 mmol) of 2-adamantylidenepropene in 20 mL of  $\text{CH}_2\text{Cl}_2$  was added 270 mg of *N*-chlorosuccinimide. After being stirred for 0.75 h at room temperature, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , washed with water, dried over  $\text{MgSO}_4$ , and evaporated. A quantitative yield of 1-chloro-1-(2-propenyl)adamantane was obtained:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.0 (br s, 1 H), 5.1 (br s, 1 H), 2.7–1.4 (br m, 14 H), 1.72 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  146.2 (s), 112.6 (t), 82.4 (s), 18.6 (q), and six lines between 37.9 and 26.5.

Chromatography over  $\text{SiO}_2$  with  $\text{CH}_2\text{Cl}_2$  afforded in 78% yield the allylic rearrangement product, 2-adamantylidene-1-chloropropene:  $n_D^{20}$  1.5407°;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.1 (s, 2 H), 3.05–2.7 (br m, 2 H), 1.73 (s, 3 H), 2.0–1.6 (br, 12 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  148.1 (s), 117.5 (s), 46.3 (t), 15.9 (q), and six lines between 38.9 and 27.7; mass spectrum,  $m/e$  210:212 (3:1); exact mass calcd  $m/e$  210.116, found 210.115. The NMR spectra indicated the presence of ~5% unrearranged product.

**2-Chloro-2,3-dimethylbut-1-ene.** To a solution of 500 mg of 2,3-dimethylbut-2-ene in 20 mL of  $\text{CH}_2\text{Cl}_2$  was added 800 mg *tert*-butyl hypochlorite. After the reaction mixture was stirred at room temperature for 0.5 h, the  $\text{CH}_2\text{Cl}_2$  was evaporated with great care. The  $^1\text{H}$  NMR spectrum indicated, besides *tert*-butyl alcohol and the excess *tert*-butyl hypochlorite, complete conversion of 2,3-dimethylbut-2-ene to 2-chloro-2,3-dimethylbut-1-ene. No attempts were made to get the product pure in a high yield. A sample was obtained by distillation:  $n_D^{20}$  1.4378° (lit.<sup>9</sup>  $n_D^{20}$  1.4380°);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.95 (br s, 1 H), 4.75 (br s, 1 H), 1.84 (s, 3 H), 1.6 (s, 6 H).

**4,4'-Di-*tert*-butyl-1,1'-bicyclohexenyl.** To a stirred solution of *syn*-4,4'-di-*tert*-butylcyclohexylidene-cyclohexane (272 mg, 1 mmol) in 20 mL of  $\text{CH}_2\text{Cl}_2$  was added 150 mg of *N*-chlorosuccinimide. After being stirred for 0.75 h, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , washed with water, dried over  $\text{MgSO}_4$ , and evaporated. The yield of the two isomers of 4,4'-di-*tert*-butyl-1,1'-bicyclohexenyl was 260 mg (96%): mp 140–148 °C (after crystallization from 1,4-dioxane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.9–5.6 (br m, 2 H), 2.5–0.9 (br, 12 H), 0.83 (s, 18 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  136.3 (s), 136.1 (s), 121.6 (d), 121.2 (d), and seven signals between 44.0 and 24.3. The product was the same as the dehydrated

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product from the pinacol coupling of 4-*tert*-butylcyclohexanone.<sup>33</sup>

**Reaction of *tert*-Butyl Hypochlorite with *syn*-, *anti*-, and *syn/anti*- (1:1) 4,4'-Di-*tert*-butylcyclohexylidene-cyclohexane.** To a stirred solution of 272 mg of *syn* olefin in 1.5 mL of C<sub>6</sub>D<sub>6</sub> was added 110 mg of *tert*-butyl hypochlorite in 0.5 mL of C<sub>6</sub>H<sub>6</sub>. The reaction mixture was stirred at room temperature for 1 h. <sup>1</sup>H NMR indicated a total conversion of the olefin to the two 1-(4-*tert*-butyl-1-cyclohex-1-enyl)-4-*tert*-butyl-1-chloro-cyclohexane in the ratio 2:1. The <sup>1</sup>H NMR spectrum is almost identical with the <sup>1</sup>H NMR spectrum of the corresponding hydroxy compounds, obtained by NaBH<sub>4</sub> reduction of the hydro-

peroxide. The latter was obtained via <sup>1</sup>O<sub>2</sub> oxygenation of the *syn* or *anti* olefin. Standing at room temperature in C<sub>6</sub>D<sub>6</sub>, both allylic chlorides afforded the diene within several hours. The <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) data of the two allylic chlorides are as follows: δ 6.05–5.7 (br, 1 H), 2.7–1.3 (br, 14 H), 0.98 (s), 0.92 (s), 0.89 (s), 0.83 (s); the last four signals were integrated for 18 H and have a ratio 2:2:1:1, as well for the *syn*, *anti*, and *syn/anti* (1:1) compounds.

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## Thermal Decomposition of Some Perfluoro- and Polyfluorodiacyl Peroxides

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Seven polyfluoroacyl peroxides were synthesized, some of them by a new procedure involving the direct interaction of an acyl fluoride with hydrogen peroxide. In the temperature range of 20–40 °C, all these peroxides undergo first-order decomposition in dilute 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) solutions (≤0.02 M.). The major decomposition products were separated and characterized as the coupling products of the corresponding radicals, R<sub>F</sub>·-R<sub>F</sub>·. Differing from other perfluoro or polyfluoro radicals, the perfluoro- $\alpha$ -isopropoxyethyl radicals (10) undergo substantial  $\beta$  scission to form perfluoroisopropyl radicals (11) during their lifetime. The  $\Delta H^\ddagger$  values for the perfluoroacyl peroxides are about 24 kcal mol<sup>-1</sup>, or about 5 kcal lower than that of the nonfluorinated diacyl peroxides (~29 kcal mol<sup>-1</sup>). Apparently, the higher relative rates for 3 and 7 are caused by different factors. The latter peroxide (7) decomposes with a more favorable  $\Delta S^\ddagger$  term, whereas the former (3) decomposes with lower values of both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ . Thus, weakening of the peroxide bond by H bonding of the peroxide oxygen atom with the acidic  $\omega$ -hydrogen atom seems to be implicated in the decomposition of 3. With a half-life of 81 min at 20 °C, 3 may become a useful low-temperature initiator for free-radical reactions and polymerization.

Both theoretical and practical interests have unceasingly kept the research on diacyl peroxides active for many years. One important theoretical theme has been the mechanistic pathways of their decomposition, whether ionic or free radical or whether concerted or stepwise, in cases where homolysis pertains. Other aspects of interests concern themselves with structural and environmental effects on the rates and mechanistic paths of decomposition. The subject has been comprehensively reviewed by Hiatt<sup>2</sup> and Koenig,<sup>3</sup> the impact of ESR and CIDNP on this branch of research is also well-known.<sup>4,5</sup>

Most of all of the diacyl peroxides which had been investigated are hydrocarbon derivatives. Relatively few fluoro- or perfluorodiacyl peroxides are known, and available kinetic data are few.<sup>6,7</sup> Since they have been

used as initiators for polymerization of fluoro olefins for years<sup>8</sup> and they possess distinct structural characteristics, research on synthetic and mechanistic aspects of these compounds may yield useful information on both basic knowledge and practical applications.

Barium peroxide, sodium peroxide, and hydrogen peroxide have been used for the synthesis of perfluorodiacyl peroxides;<sup>10,11</sup> the last two reagents were used in this work. In preparing peroxides by the reaction between aqueous sodium peroxide and perfluoroacyl chlorides, we made a preliminary study on the effects of various factors on the yields of the desired products. Among these factors, e.g., the reaction temperature, the amount of water, and the Na<sub>2</sub>O<sub>2</sub>/R<sub>F</sub>COCl molar ratio, the last one appeared rather important, and a value of 0.4–0.5 was preferred. When H<sub>2</sub>O<sub>2</sub> was used in place of Na<sub>2</sub>O<sub>2</sub>, the procedure became even more convenient for the aqueous-organic two-phase system used. This procedure has been successfully adapted to the syntheses starting from acyl fluorides. All seven

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