Rearrangements in the halogenation of tetraalkylethylenes with N-halosuccinimides and tert-butyl hypochlorite

ARTICLE *in* THE JOURNAL OF ORGANIC CHEMISTRY · MAY 1982

Impact Factor: 4.72 · DOI: 10.1021/jo00132a006

3 AUTHORS, INCLUDING:

Richard M. Kellogg
Syncom
403 PUBLICATIONS **10,483** CITATIONS

SEE PROFILE

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 CH_2N_2 in dry ether affords quantitatively the product **2**: IR ($CHCl_3$) 1705, 1620 cm^{-1}; NMR ($CDCl_3$, 360 MHz; for the spectral data of the C- and D-ring protons see Table I) δ 3.85 (s, 3 H, 2-OCH_3), 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 M^+ *m/e* 258.1368, found *m/e* 258.1368.

6-Carbethoxy-6,7-diaza-2-methoxy-8-methylgibban-10-one (8). Compound **2** (1 mmol, 0.258 g), 1 mmol (0.108 g) of ClCOOEt, and 1 mmol (0.101 g) of NEt_3 are dissolved in 15 mL of dry CH_2Cl_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–acetonitrtile (85/15), which affords 0.90 mmol (0.297 g) of **8**. Recrystallization from benzene–hexane gives white crystals: mp 149 °C; IR ($CHCl_3$) 1725 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.35 (t, 3 H, OCH_2CH_3), 1.42 (d, 3 H, 8-CH_3), 1.98 (dd, 1 H, $J_{9_A9_B}$ = 12 Hz, J_{9_B8} = 7.2 Hz, 9_B-H), 2.12 (ddd, 1 H, $J_{9_A9_B}$ = 12 Hz, J_{9_A8} = 7.5 Hz, $J_{9_A11_B}$ = 2.2 Hz, 9_A-H), 2.97 (t, 1 H, $J_{5_B5_A}$ = 11.5 Hz, J_{5_B4b} = 11 Hz, 5_B-H), 2.97 (d, 1 H, $J_{11_A11_B}$ = 12.5 Hz, 11_A-H), 3.10 (dt, 1 H, $J_{11_B11_A}$ = 12.5 Hz, $J_{11_B9_A}$ = 2.2 Hz, J_{11_B8} = 1.3 Hz, 11_B-H), 3.30 (m, 1 H, 8-H), 3.32 (dd, 1 H, J_{4b5_B} = 11 Hz, J_{4b5_A} = 7.6 Hz, 4b-H), 3.72 (s, 3 H, 2-OCH_3), 4.16 and 4.32 (**ABX**$_3$ pattern, 2 H, J_{AB} = 11 Hz, OCH_2CH_3), 4.51 (dd, 1 H, $J_{5_A5_B}$ = 11.5 Hz, J_{5_A4b} = 7.6 Hz, 5_A-H), 7.2–7.5 (m, 3 H, 1-H, 3-H, 4-H); ^{13}C NMR ($CDCl_3$, 20.1 MHz) 14.9 (OCH_2CH_3), 21.6 (8-CH_3), 41.7 (5-CH_2), 43.2 (9-CH_2), 45.4 (4b-CH), 55.2 (11-CH_2), 55.9 (2-OCH_3), 58 (9a-C), 62.1 (OCH_2CH_3), 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 M^+ *m/e* 330.1579, found *m/e* 330.1581.

Acknowledgment. We are indebted to the Instituut tot aanmoediging van Wetenschappelijk Onderzoek in Nijverheid en Landbouw for a predoctoral fellowship (to L.H.) and to the FKFO for financial support. Professor M. Anteunis is acknowledged for the 360-MHz ^1H NMR spectra. We are also grateful to Dr. F. Compernolle for mass spectral analysis and to R. DeBoer and P. Valvekens for technical assistance.

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

E. W. Meijer, Richard M. Kellogg, and Hans Wynberg*

Department of Organic Chemistry, University of Groningen, 9747 AG Groningen, The Netherlands

Received July 6, 1981

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[1,2] of tetraalkylethylenes with *N*-halosuccinimides and *tert*-butyl hypochlorite. These reagents are well-known to give allylic halogenation in a radical-chain reaction.[3] 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 benzenesulfenyl chloride to give 4(e)-chloroadamantylideneadamantane (**2**) via an ionic pathway without any addition to the double bond.[4,5] In an attempt to carry out radical chlorination, **1** was treated with 1 equiv of *N*-chlorosuccinimide (NCS) in boiling CCl_4 containing a radical initiator. To our surprise the sole product was **2**. When this reaction was repeated in CH_2Cl_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 CCl_4, $CHCl_3$, or CH_2Cl_2/CH_3COOH and the rate increases with increasing solvent polarity.[6] The same product **2** was obtained when

(1) House, H. O. "Modern Synthetic Reactions"; W. A. Benjamin: Menlo Park, 1972; pp 479–488.

(2) Schmid, G. H.; Garrett, D. G. In "The Chemistry of Double-Bond Functional Groups"; Patai, S., Ed.; Wiley: London, 1977; pp 725–912.

(3) (a) March, J. "Advances in Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 636–638. (b) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; pp 347–396. (c) Walling, C.; Thaler, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877–3884. (d) Djerassi, C. *Chem. Rev.* **1948**, *43*, 271–317. (e) Skell, P. W.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381–387.

(4) Wieringa, J. H.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1970**, 4579–4582.

(5) Bolster, J. M.; Kellogg, R. M.; Meijer, E. W.; Wynberg, H. *Tetrahedron Lett.* **1979**, 285–286.

(6) (a) We observe quantitatively that the reaction rates, in general, increase progressing from CCl_4 to C_6H_6 to $CHCl_3$ to CH_2Cl_2/CH_3CO_2H. In the last two solvents the rates are most often too fast to be measured by ^1H NMR. The rates in CCl_4 and C_6H_6 vary from 3 to 15 min, depending on substrate and halogenating agent. In the cases of NBS and NCS, solubility problems had to be taken into account. (b) With an excess of NCS overchlorination occurs: 2 equiv of NCS affords a mixture of dichloroadamantylideneadamantanes, the selectivity claimed in the reaction of **1** with SCl_2 is not found: Tolstikov, G. A.; Lerman, B. M.; Umanskaya, L. I.; Struchkov, Y. T.; Espenbetov, A. A.; Yanovsky, A. L. *Tetrahedron Lett.* **1980**, *21*, 4189–4192.

0022-3263/82/1947-2005$01.25/0

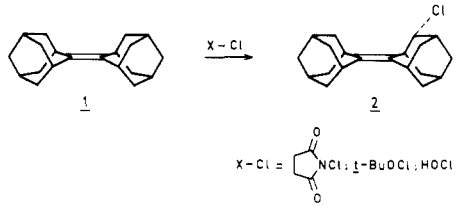

Figure 1.

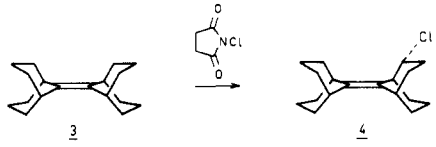

Figure 2.

tert-butyl hypochlorite (TBHC) or the combination $NaOCl/CH_3COOH$ 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)-bromoadamantylideneadamantane 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 vigourous conditions, no reaction took place.[7]

A tetraalkylethylene closely related to **1** is bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**3**).[8] 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 ^1H NMR) amounts of the thermodynamically more stable allylic isomer, 1-chloro-2,3-dimethyl-2-butene.[9,10] A tetraalkylethylene, offering both reaction types, namely, homoallylic chlorination and allylic chlorination with the double bond shift, is 2-adamantylidenepropane (**7**).[11] The olefin **7** reacts similarly to **5** to furnish **8** in quantitative yield. The latter easily rearranges to **9**, when passed through a SiO_2 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 ($^1O_2$) addition to olefins (ene reaction), as outlined for the transformation of **5** into **10**.[12] A structural link between

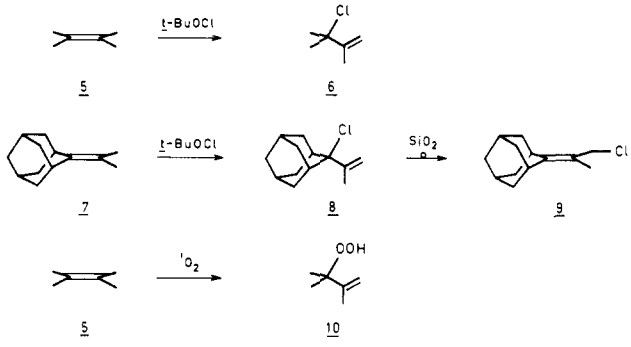

Figure 3.

the chlorinations reported here and the ene reaction of $^1O_2$ 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.[13,14] This result was offered as evidence against a concerted mechanism for the ene reaction of $^1O_2$ with alkenes. We have examined the reaction of the same olefins with TBHC; when TBHC was used in C_6D_6 solution, the only products observed were the allylic chlorides **13** and **14** in a ratio 2:1 as determined by ^1H 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.[3] An exception must be made for the reaction of these reagents in alcoholic solvents and Me_2SO-H_2O, in which addition to the double bond occurs in an electrophilic fashion.[15] Two halogenations with shift of the double bond are known in steroid chemistry, although this shift is favored by the formation of an α,β-unsaturated ketone,[16,17] as is shown for the conversion of **16** into **17**[16] (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.[1,3] 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

(7) We are interested in substituted adamantylideneadamantanes for their use as precursors for chemiluminescent probes and labels: Wynberg, H.; Meijer, E. W.; Hummelen, J. C. "Bioluminescence and Chemiluminescence"; McElroy, W. D., DeLuca, M. A., Ed.; Academic: New York, 1981, pp 687–689.

(8) (a) Bartlett, P. D.; Baumstark, A. L.; Shapiro, M. J., unpublished work, 1975. (b) Keul, H. *Chem. Ber.* **1975**, *108*, 1207–1217.

(9) 3-Chloro-2,3-dimethyl-1-butene was obtained by HCl addition to 2,3-dimethylbutadiene: Said, E. Z.; Tripping, A. E. *J. Chem. Soc., Perkin Trans 1* **1972**, *16*, 1986–1991.

(10) 3-Chloro-2,3-dimethyl-1-butene was also obtained by Cl_2 addition to 2,3-dimethyl-2-butene: Taft, R. W., Jr. *J. Am. Chem. Soc.* **1948**, *70*, 3364–3369.

(11) Landa, S.; Vais, J.; Burkhard, J. *Collect. Czech. Chem. Comm.* **1967**, *32*, 570–575.

(12) (a) Schenk, G. O.; Schulte-Elte, K. *Justus Liebigs Ann. Chem.* **1958**, *618*, 185–193. For review of singlet oxygen reactions, see: (b) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133–336. (c) Wasserman, H. H.; Murray, R. W. "Singlet Oxygen"; Academic Press: London, 1979.

(13) Kellogg, R. M.; Kaiser, J. K. *J. Org. Chem.* **1975**, *40*, 2575–2576.

(14) Kellogg, R. M.; Nooteboom, M.; Kaiser, J. K. *J. Org. Chem.* **1975**, *40*, 2573–2575; *Tetrahedron* **1976**, *32*, 1641–1648.

(15) Dalton, D. R.; Dutta, V. P.; Jones, D. C. *J. Am. Chem. Soc.* **1968**, *90*, 5498–5501.

(16) (a) Mukawa, F.; Dorfman, R. I.; Ringold, H. J. *Steroids* **1963**, *1*, 9–20. (b) Viger, A.; Coustal, S.; Marquet, A. *J. Am. Chem. Soc.* **1981**, *103*, 451–458.

(17) The reaction of TBHC with cholesterol is best explained via an ionic pathway: Ginsburg, D. *J. Am. Chem. Soc.* **1953**, *75*, 5489–5491. Anbar, M.; Ginsburg, D. *Chem. Rev.* **1954**, 925–958.

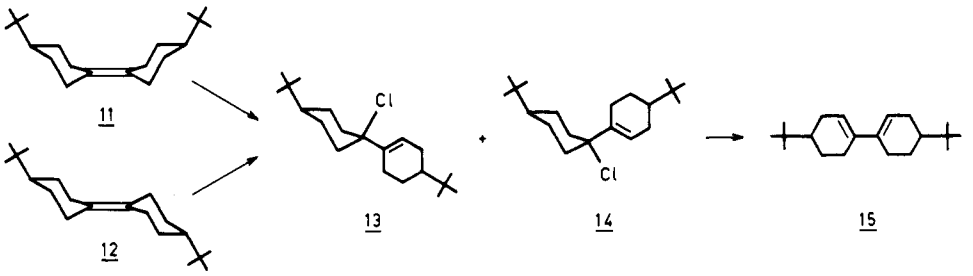

Figure 4.

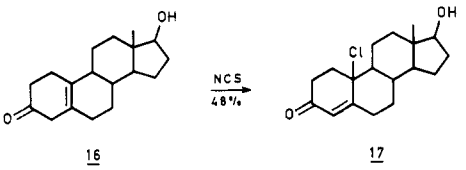

Figure 5.

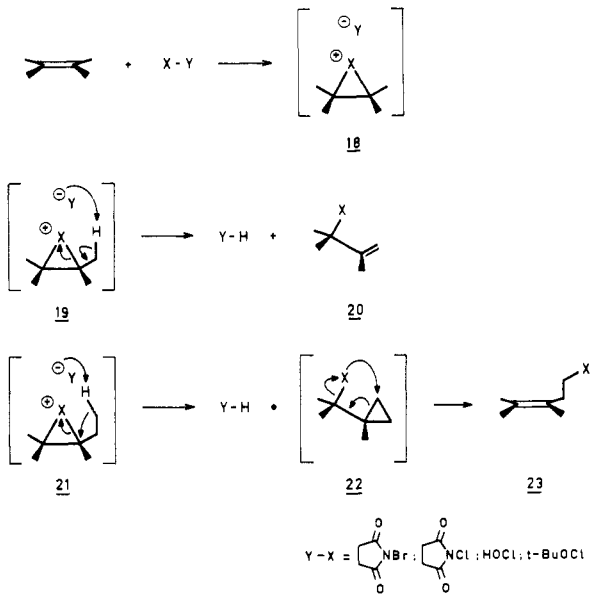

Figure 6.

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.[18] 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.[19] Noteworthy is the high yield of **6** from **5** under these conditions.[10]

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 α-halocyclopropane **22**. The latter rearranges easily to the stable **23**, in which the halide occupies the equatorial

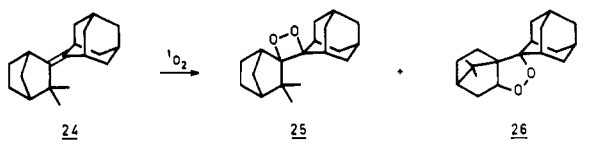

Figure 7.

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.[20,21] In addition, the major product in the bromination of norbornene in Me_2SO with NBS is an α-bromocyclopropane derivative.[22] The formation of a cyclopropane in the adamantane skeleton and the stereoselective addition to this dehydroadamantane have been reported previously.[23] 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.[24] Two other routes to **2** have been reported. The decomposition of the chloronium ion of **1** affords **2** in moderate yield.[4] 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.[4,25] Secondly, the interaction of benzenesulfenyl chloride with **1**, furnishing **2** in high yield (85%), is explained on the basis of a dehydroadamantane intermediate.[5]

Noteworthy is the striking resemblance of these chlorinations to the singlet oxygen ($^1O_2$) additions.[8] The structural consequence—introduction of a heteroatom with shift of the double bond—is identical. Moreover the stereochemical aspects of the $^1O_2$ ene reaction and the chlorinations described here are clearly related as outlined for the syn and anti olefins **11** and **12**.[10] This similarity needs stressing in view of the "one of a kind" discussions often encountered in analysis of the mechanism of $^1O_2$ reactions. Central in these discussions are often the perepoxide or the open zwitterionic intermediates.[26] In halonium ion chemistry in which the structures could be studied by ^1H and ^{13}C NMR spectroscopy,[27] a bridged structure is pro-

(18) (a) An ionic component in the reaction of chlorine with cyclohexene has been noted previously: Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 2161–2171, 2172–2183. (b) Fahey, R. C.; Schubert, C. *J. Am. Chem. Soc.* **1965**, *87*, 5172–5179.

(19) Poutsma, M. L. *Science* **1967**, *157*, 997–1005.

(20) Olah, G. A.; Schilling, P.; Westerman, P. W.; Lin, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 3581–3589.

(21) Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907–908.

(22) Dalton, D. R.; Rodebaugh, R. K.; Jefford, C. W. *J. Org. Chem.* **1972**, *37*, 362–367.

(23) (a) Udding, A. C.; Strating, J.; Wynberg, H.; Schlatmann, J. L. M. A. *J. Chem. Soc., Chem. Commun.* **1966**, 657–658. (b) Udding, A. C.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1968**, 1345–1350.

(24) Young, W. G.; Winstein, S.; Goering, H. L. *J. Am. Chem. Soc.* **1951**, *73*, 1958–1963.

(25) Fort, R. C., Jr. "Adamantane"; Marcel Dekker: New York, 1976; p 179.

(26) (a) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419–425. (b) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359–387 (see also ref 9). (c) Harding, L. B.; Goddard, W. A., III, *J. Am. Chem. Soc.* **1980**, *102*, 439–449.

(27) Olah, G. A. "Halonium Ions"; Wiley: New York, 1975. See also: Freeman, F. *Chem. Rev.* **1975**, *75*, 439–490.

posed for a symmetrically substituted olefin (in terms of $^1O_2$ chemistry: the perepoxide). An "open" α-halo cation has been established for an unsymmetrically substituted olefin (in terms of $^1O_2$ chemistry: the zwitterionic peroxide). The electronic properties of the substitutents 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 $^1O_2$ with (silyl)enol ethers.[28] An analogy to the homoallylic halogenation *may* also exist in $^1O_2$ chemistry, namely, in the remarkable rearrangement in the $^1O_2$ addition to tetraalkylethylene **24** found by McCapra.[29] 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.[7,8] The structural aspects of the rearrangement observed during this halogenations 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. ^1H NMR spectra were recorded at 60 MHz (Varian A-60 or Hitachi Perkin-Elmer R-24 B). ^1H chemical shifts are reported in δ units (parts per million) relative to $CHCl_3$ and converted to δ Me_4Si values, using $\delta(CHCl_3) = 7.25$ ppm. ^{13}C NMR spectra were recorded at 25 MHz (Varian XL-100) and ^{13}C chemical shifts are denoted in δ units (parts per million) relative to the solvent $CDCl_3$ and converted to δ Me_4Si values, using $\delta(CDCl_3) = 76.9$ 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 $NaOCl/CH_3COOH$ were obtained commercially and used as such. TBHC was prepared according to a published procedure.[30]

Tetraalkylethylenes. The tetraalkylethylenes, adamantylideneadamantane (**1**),[31] bicyclo[3.3.1]nonylidenebicyclo[3.3.1]-nonane (**3**),[32] 2-adamantylidenepropane (**7**),[11] *syn*- and *anti*-4,4′-di-*tert*-butylcyclohexylidenecyclohexane (**11** and **12**)[14] 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 CH_2Cl_2 was added 1.05 mmol (140 mg) of *N*-chlorosuccinimide. The reaction mixture was stirred for 1 h at room temperature, diluted with CH_2Cl_2, and washed twice with water. The organic layer was dried over $MgSO_4$ and evaporated. The yield of 4-(e)-chloroadamantylideneadamantane was 300 mg (98%): mp 142–143 °C (lit.[4,5] mp 144–145 °C); ^1H NMR ($CDCl_3$) δ 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 CH_2Cl_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 CH_2Cl_2 and washed twice with water and a saturated $Na_2S_2O_3$ solution. The organic layer was dried over $MgSO_4$ 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; ^1H NMR ($CDCl_3$) δ 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}C NMR ($CDCl_3$) δ 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 CH_2Cl_2 was added 115 mg (0.86 mmol) of *N*-chlorosuccinimide. The reaction mixture was refluxed and stirred for 1 h and CH_2Cl_2 was added to dilute the reaction mixture. The organic layer was washed twice with water, dried over $MgSO_4$, 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, Al_2O_3) and sublimation [45 °C (0.01 mm)]: mp 50–53 °C; ^1H NMR ($CDCl_3$) δ 4.4–3.9 (m, 1 H), 3.1 (br s, 1 H), 2.85 (br s, 3 H), 2.5–1.2 (br, 22 H); ^{13}C NMR ($CDCl_3$) δ 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-Adamantylidenepropane. To a stirred solution of 208 mg (1 mmol) of 2-adamantylidenepropane in 20 mL of CH_2Cl_2 was added 270 mg of *N*-chlorosuccinimide. After being stirred for 0.75 h at room temperature, the reaction mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and evaporated. A quantitative yield of 1-chloro-1-(2-propenyl)adamantane was obtained: ^1H NMR ($CDCl_3$) δ 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}C NMR ($CDCl_3$) δ 146.2 (s), 112.6 (t), 82.4 (s), 18.6 (q), and six lines between 37.9 and 26.5.

Chromatography over SiO_2 with CH_2Cl_2 afforded in 78% yield the allylic rearrangement product, 2-adamantylidene-1-chloropropane: n^{20}_D 1.5407°; ^1H NMR ($CDCl_3$) δ 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}C NMR ($CDCl_3$) δ 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 CH_2Cl_2 was added 800 mg *tert*-butyl hypochlorite. After the reaction mixture was stirred at room temperature for 0.5 h, the CH_2Cl_2 was evaporated with great care. The ^1H 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-dimethyl-but-1-ene. No attempts were made to get the product pure in a high yield. A sample was obtained by distillation: n^{20}_D 1.4378° (lit.[9] n^{20}_D 1.4380°); ^1H NMR ($CDCl_3$) δ 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*-butylcyclohexylidenecyclohexane (272 mg, 1 mmol) in 20 mL of CH_2Cl_2 was added 150 mg of *N*-chlorosuccinimide. After being stirred for 0.75 h, the reaction mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, 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); ^1H NMR ($CDCl_3$) δ 5.9–5.6 (br m, 2 H), 2.5–0.9 (br, 12 H), 0.83 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 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

(28) (a) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6437–6445. (b) Asveld, E. W. H.; Kellogg, R. M. *Ibid.* **1980**, *102*, 3644–3645.

(29) (a) McCapra, F.; Behesthi, I. *J. Chem. Soc., Chem. Commun.* **1977**, 517–518. (b) Hitchcock, P. B.; Behesthi, I. *J. Chem. Soc., Perkin Trans 2* **1979**, 126–129.

(30) Mintz, M. J.; Walling, C. "Organic Syntheses", Collect. Vol. 5; Wiley: New York, 1973; pp 184–187.

(31) Bartlett, P. D.; Ho, M. S. *J. Am. Chem. Soc.* **1974**, *96*, 627–629.

(32) McMurry, J. E.; Flemming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708–4709.

product from the pinacol coupling of 4-*tert*-butylcyclohexanone.[33]

Reaction of *tert*-Butyl Hypochlorite with *syn*-, *anti*-, and *syn*/*anti*- (1:1) 4,4'-Di-*tert*-butylcyclohexylidenecyclohexane. To a stirred solution of 272 mg of syn olefin in 1.5 mL of C_6D_6 was added 110 mg of *tert*-butyl hypochlorite in 0.5 mL of C_6H_6. The reaction mixture was stirred at room temperature for 1 h. ^1H NMR indicated a total conversion of the olefin to the two 1-(4-*tert*-butyl-1-cyclohex-1-enyl)-4-*tert*-butyl-1-chlorocyclohexane in the ratio 2:1. The ^1H NMR spectrum is almost identical with the ^1H NMR spectrum of the corresponding hydroxy compounds, obtained by $NaBH_4$ reduction of the hydroperoxide. The latter was obtained via $^1O_2$ oxygenation of the syn or anti olefin. Standing at room temperature in C_6D_6, both allylic chlorides afforded the diene within several hours. The ^1H NMR (C_6D_6) 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.

(33) Asveld, E. W. H. Dissertation, Groningen, 1980.

Registry No. 1, 30541-56-1; 2, 79732-69-7; 3, 55993-21-0; 4, 80287-95-2; 5, 563-79-1; 6, 37866-05-0; 7, 20441-18-3; 8, 80287-96-3; 9, 80287-97-4; 11, 56577-76-5; 12, 56577-77-6; 13, 80287-98-5; 14, 80287-99-6; 15, 80288-00-2; NCS, 128-09-6; NBS, 128-08-5; 4(e)-bromoadamantylideneadamantane, 80288-01-3; TBHC, 507-40-4; *N*-iodosuccinimide, 516-12-1.

Thermal Decomposition of Some Perfluoro- and Polyfluorodiacyl Peroxides

Zhao Chengxue, Zhou Renmo, Pan Heqi, Jin Xiangshan, Qu Yangling, Wu Chengjiu,* and Jiang Xikui[1]

Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai 200032, China

Received October 30, 1980

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 ($\lesssim$0.02 M.). The major decomposition products were separated and characterized as the coupling products of the corresponding radicals, R_F–R_F. Differing from other perfluoro or polyfluoro radicals, the perfluoro-α-isopropoxyethyl radicals (10) undergo substantial β scission to form perfluoroisopropyl radicals (11) during their lifetime. The $\Delta H^{\ddagger}$ values for the perfluoroacyl peroxides are about 24 kcal mol^{-1}, or about 5 kcal lower than that of the nonfluorinated diacyl peroxides ($\sim$29 kcal mol^{-1}). 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 ω-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[2] and Koenig;[3] the impact of ESR and CIDNP on this branch of research is also well-known.[4,5]

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.[6,7] Since they have been used as initiators for polymerization of fluoro olefins for years[8] 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;[10,11] 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_2O_2/R_FCOCl molar ratio, the last one appeared rather important, and a value of 0.4–0.5 was preferred. When H_2O_2 was used in place of Na_2O_2, 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

(1) Formerly spelled Jiang Hsi-Kwei, Chiang Hsi-Kwei, or Stanley Hsi-Kwei Jiang (Chiang).
(2) R. Hiatt in "Organic Peroxides", Vol. 1, D. Swern, Ed., Wiley, New York, 1970, p 799.
(3) T. W. Koenig in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, 1973, p 113.
(4) J. K. Kochi in "Free Radicals", Vol. 2, J. K. Kochi, Ed., Wiley, New York, 1973, p 698.
(5) See, e.g., R. G. Lawler in "Chemically Induced Magnetic Polarization", L. T. Muus et al Eds., D. Reidel, Boston, 1977, p 17.
(6) Ronald A. DeMarco and Jeanne M. Shreeve, *Adv. Inorg. Chem. Radiochem.* 16, 109 (1974).
(7) V. A. Novikov, V. P. Sass, L. S. Ivanova, L. F. Sokolov, S. V. Sokolov, *Vysokomol. Soedin., Ser. A.*, 17, 1235 (1975).
(8) (a) U.S. Patent 2700662 (1955); *Chem. Abstr.*, 49, 5886*i* (1955); (b) British Patent 781532 (1958); *Chem. Abstr.*, 52, 1684*c* (1958); (c) U.S. Patent 2943080 (1960); *Chem. Abstr.*, 54, 20399*d* (1960); (d) German Offen. 1806426 (1969); *Chem. Abstr.*, 71, 13533*s* (1969).
(9) B. C. Brodie, *J. Chem. Soc.*, 17, 266 (1864).
(10) C. C. Price and E. Krebs "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 649.
(11) P. E. Rice, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Sci.*, 12(1), 396 (1971).

0022-3263/82/1947-2009$01.25/0