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(3)-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 one reaction and the causes of this resemblance are discussed.

In this paper we describe the remarkable halogenation of tetraalkylethylenes with N-halosuccinimides and tert-butyl hypochlorite. These reagents are well-known to give allylic halogenation in a radical-chain reaction. 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.

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Rearrangements in the Halogenation of Tetraalkylethylenes with \textit{N}-Halosuccinimides and \textit{tert}-Butyl Hypochlorite

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The chlorinations reported here and the ene reaction of $\mathrm{O_2}$ 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. This result was offered as evidence against a concerted mechanism for the ene reaction of $\mathrm{O_2}$ with alkenes. We have examined the reaction of the same olefins with TBHC; when TBHC was used in $\mathrm{CD}_2$ solution, the only products observed were the allylic chlorides 13 and 14 in a ratio 2:1 as determined by $^1$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'-bicyclohexanyle (15, Figure 4).

Discussion

The results presented here provide strong evidence for the ionic reaction of NCS, NBS, and TBHC with tetraalkylenes. 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 monoalkylated alkenes, radical initiators (light or peroxides) are needed, resulting in halogenation at the allylic position to form usually the thermodynamically most stable product in excess.2 An exception must be made for the reaction of these reagents in alcoholic solvents and Me$_2$SO- H$_2$O, 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 $\alpha,\beta$-unsaturated ketone,16,17 as is shown for the conversion of 16 into 17 (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.12 However, when the olefins are electron-rich as is the case in tetraalkylenes 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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1. tert-butyl hypochlorite (TBHC) or the combination NaOCl/CH$_2$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)-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 vigorous conditions, no reaction took place.1

A tetraalkylethylene closely related to 1 is bicyclo[3.3.1]nonylidenecyclo[3.3.1]nonane (3). 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 homoallyl 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 reacts spontaneously and quantitatively with NCS and TBHC, forming 

2,3-dimethylbutadiene: Said, E. A. J. Org. Chem. 1975, 40, 2575-2576. (12) A tetraalkylethylene closely related to 1 is bicyclo[3.3.1]nonylidenecyclo[3.3.1]nonane (3). 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).

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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 ($^1\mathrm{O}_2$) addition to olefins (ene reaction), as outlined for the transformation of 5 into 10.12 A structural link between

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Figure 4.

Figure 5.

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 (Figure 7). Intermediates described here are clearly related to the stereoselective addition to this dehydroadamantane intermediate.

Noteworthy is the high yield of 2 from 5 under these conditions.

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 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. In addition, the major product in the bromination of norbornene in Me2SO with NBS is an α-bromocyclopropane derivative. The formation of a cyclopropane in the adamantane skeleton and the stereoselective addition to this dehydroadamantane have been reported previously. Moreover the rearrangement of 22 into 23 probably takes place via a not completely free carbocation since otherwise acetate formation would have occurred in the presence of acetic acid as cosolvent. Two other routes to 2 have been reported. The decomposition of the chloronium ion of 1 affords 2 in moderate yield. 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. Secondly, the interaction of benzenesulfenyl chloride with 1, furnishing 2 in high yield (85%), is explained on the basis of a dehydroadamantane intermediate.

Noteworthy is the striking resemblance of these chlorinations to the singlet oxygen (O2) additions. The structural consequence—introduction of a heteroatom with shift of the double bond—is identical. Moreover the stereochemical aspects of the O2ene reaction and the chlorinations described here are clearly related as outlined for the syn and anti olefins 11 and 12. This similarity needs stressing in view of the “one of a kind” discussions often encountered in analysis of the mechanism of O2 reactions. Central in these discussions are often the perepoxide or the open zwitterionic intermediates. In halonium ion chemistry in which the structures could be studied by 1H and 13C NMR spectroscopy, a bridged structure is pro-

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(18) (a) An ionic component in the reaction of chlorine with cyclohexene has been noted previously: Poutama, M. L. J. Am. Chem. Soc. 1965, 87, 5172-5179.
(b) Primmer, A. A. Chem. Rev. 1979, 79, 359-387 (see also ref 9).
posed for a symmetrically substituted olefin (in terms of \( \text{O}_2 \) chemistry: the peroxyde). An "open" \( \alpha \)-halo cation has been established for an unsymmetrically substituted olefin (in terms of \( \text{O}_2 \) chemistry: the zwitterionic peroxye). 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 peroxyde is quenched in the reaction of \( \text{O}_2 \) with (silyl)enol ethers.\(^{28}\) An analog to the homolytic halogenation may also exist in \( \text{O}_2 \) chemistry, namely, in the remarkable rearrangement in the \( \text{O}_2 \) addition to tetralakyllethylene 24 found by McCapra.\(^{29}\) This rearrangement furnishes dioxdioxane 26, which can be formed by a homolytic 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 tetralakyllethlenes with \( N \)-halosuccinimides on tert-butyl hypochlorite. These reactions furnish in high yield starting materials used subsequently in the synthesis of stable 1,2-dio~etanes.\(^{\text{4708-4709.}}\) The structural genations bear an obvious resemblance to the allylic rearrangement observed during this halo

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Experimenat Section

Instrumentation. Melting points were determined on a Mettler FP2 melting point apparatus. IR spectra were recorded on a Unicam (SP-200) spectrophotometer. \(^{1}H\) NMR spectra were recorded at 60 MHz (Varian A-60 or Hitachi Perkin-Elmer R-24 B). \(^1H\) Chemical shifts are reported in \( \delta \) units (parts per million) relative to CHCl3 and converted to \( \delta \text{Me}_{2}Si \) values, using \( \delta \text{(CHCl}_{3} \) = 7.25 ppm. \(^13C\) NMR spectra were recorded at 25 MHz (Varian XL-100) and \(^{13}C\) chemical shifts are denoted in \( \delta \) units (parts per million) relative to the solvent CDCl3 and converted to \( \delta \text{Me}_{2}Si \) 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 NaCl/CH3COOH were obtained commercially and used as such. \( \text{TBHC} \) was prepared according to a published procedure.\(^{30}\)

Tetraalkylethlenes. The tetraalkylethlenes, adamantylidenepropane: \(^{47} \) to a stirred solution of \( 500 \text{ mg of} \) adamantylidenepropane in \( 40 \text{ mL of} \) CH2Cl2 was added 140 mg of N-chlorosuccinimide. After being stirred for \( 0.75 \text{ h} \) at room temperature, the reaction mixture was diluted with CH2Cl2, washed with water, and evaporated. The yield of 4-(\( N \)-chlorobicyclo[3.3.1]nonynylidenebicyclo[3.3.1]nonane was 260 mg (98%): mp 93-95 \( \text{C} \); \(^{1}H\) NMR (CDCl3) \( \delta 4.15 \text{(s, 1 H), 3.05-2.7} \text{ ppm, 12 H); 13C NMR (CDCl}_{3} \) \( \delta 146.2 \text{(s), 117.5 (t), 117.5 (s), 118.6 (s), 18.6 (q), and six lines between 38.9 and 27.7}; \) mass spectrum, \( m / e \) 278/278 (31); exact mass calcd 278.180, found 278.182.

Chromatography over SiO2 with CH2Cl2 afforded in 78% yield the allylic rearrangement product, 2-adamantylidenepropane: \(^{3644-3645.}\) To a solution of \( 200 \text{ mg of} \) adamantylidenepropane in \( 20 \text{ mL of} \) CH2Cl2 was added 115 mg of \( N \)-chlorosuccinimide. After being stirred for \( 0.75 \text{ h} \) at room temperature, the reaction mixture was diluted with CH2Cl2, washed with water, and evaporated. A quantitative yield of \( 1 \)-chloro-1-(2-propenyl)adamantane was obtained: \(^{1}H\) NMR (CDCl3) \( \delta 5.0 \text{(s, 1 H), 5.1-4.9 \text{ ppm, 12 H); 13C NMR (CDCl}_{3} \) \( \delta 146.2 \text{(s), 112.6 (t), 142.4 (s), 18.6 (s), and 26.6 (q)} \) (13 lines between 38.9 and 27.7); mass spectrum, \( m / e \) 210/212 (31); exact mass calcd 210.116, found 210.115. The NMR spectra indicated the presence of ~5% unreacted product.

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2-Chloro-2,3-dimethylbut-2-ene. To a solution of \( 500 \text{ mg of} \) 2,3-dimethylbut-2-ene in \( 20 \text{ mL of} \) CH2Cl2 was added 800 mg tert-butyl hypochlorite. After the reaction mixture was stirred at room temperature for 0.5 h, the CH2Cl2 was evaporated with great care. The \(^{1}H\) NMR spectrum indicated, besides tert-butyl alcohol and the excess tert-butyl hypochlorite, complete conversion of 2-chloro-2,3-dimethylbut-2-ene. No attempts were made to purify the product. A sample was obtained by distillation: \(^{n}_{D} 1.4\) (lit. \(^{n}_{D} 1.4\) 1.43086); \(^{1}H\) NMR (CDCl3) \( \delta 4.95 \text{(s, 1 H), 4.75 (s, 1 H), 1.84 (s, 3 H), 1.6 (s, 6 H}. \)
Thermal Decomposition of Some Perfluoro- and Polyfluorodiacyl Peroxides

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Seven perfluoroacyl 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 1,1,2,2-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$_{p}$-R$_{q}$. Differing from other perfluoro or polyfluoro radicals, the perfluoro-a-isopropoxyethyl radicals (10) undergo substantial b scission to form perfluoroisopropyl radicals (11) during their lifetime. The $\Delta H^*$ values for the perfluoroacyl peroxides are about 24 kcal mol$^{-1}$, or about 5 kcal lower than that of the nonfluorinated diacyl peroxides (-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 $\Delta S^*$ term, whereas the former (3) decomposes with lower values of both $\Delta H^*$ and $\Delta S^*$. Thus, weakening of the peroxide bond by H bonding of the peroxide oxygen atom to the acrylic hydrogen atom seems to be implicated in the decomposition of 5. 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$^4$; the impact of ESR and CIDNP on this branch of research is also well-known.$^{4,5}$ Most of all 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 perfluorocayl 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 Na$_2$O$_2$/R$_2$COCl molar ratio, the last one appeared rather important, and a value of 0.4-0.5 was preferred. When H$_2$O$_2$ was used in place of Na$_2$O$_2$, 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

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(1) Formerly spelled Jiang Hsi-Kwei, Chiang Hsi-Kwei, or Stanley Hsi-Kwei Jiang (Chiang).