The standard inversion–recovery method was used to determine the spin–lattice relaxation times[8] (T_1) of each of the eight compounds (Table I).[9] The T_1 values were determined in benzene-d_6 under the conditions we were employing to analyze our samples. These numbers should not be considered to be absolute standard reference values because the solvent was not rigorously purged of oxygen; it is likely that benzene-d_6 does have an effect on the T_1 values as shown by an observed definite concentration effect. A T_1 measurement made on one sample containing 45 mg of **6** in 0.4 mL of benzene-d_6 showed a significantly longer T_1 (7.1 s) than one determined on 15 mg in the same amount of solvent (5.2 s). All subsequent analytical spectra were taken on samples containing 15 mg of compound in 0.4 mL of solvent so that the *relative* T_1 values in Table I are significant.

The observed T_1 differences[10] required that the NMR instrumental parameters be adjusted to accommodate the compound with the longest relaxation time present in the sample being analyzed. Typically, a pulse width, corresponding to a flip angle of ca. 30°, was employed,[11] with a delay time appropriate for the compound with the longest T_1 contained in a sample according to the guidelines given by Stanislawski and Van Wazer[6] for the collection of quantitative data for NMR spectra under these conditions. It was established by using standard samples that a component could be determined within 1% of its known composition and could be detected down to 0.5%.

Experimental Section

General Methods. The ^{31}P NMR spectra were taken on a Varian XL-100 spectrometer supported by a Nicolet TT100A Pulse and data system and were broad-band ^1H decoupled. The solvents used (C_6D_6 and $CDCl_3$) were purchased in 0.5-mL ampules sealed under N_2 (Aldrich) and handled in a glovebag for phosphine samples. Samples containing only phosphine oxides were prepared in air.

All samples were dissolved in 0.4 mL of C_6D_6. The phosphine oxide samples were freshly prepared with 15 mg of compound, except for one sample which contained 45 mg. The experiments on the phosphines were run on mixed sealed-tube samples containing approximately 40 mg of each phosphine.

Relaxation Time (T_1) Studies. The experiments were run automatically by a standard inversion–recovery sequence in the NTCFT software program supplied by Nicolet for its computers. After the 90° and 180° pulses were determined, values for the variable τ were supplied to the computer. The inversion–recovery sequence was run, and resulting spectra were examined. If necessary, the τ values were adjusted, and the experiment was repeated. The T_1 value was calculated on the basis that no signal appears when $\tau = \ln 2T_1$.

Registry No. **1**, 65440-73-5; **2**, 65440-74-6; **3**, 74298-25-2; **4**, 74298-24-1; **5**, 65440-75-7; **6**, 65440-76-8; **7**, 74298-26-3; **8**, 74298-27-4.

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[8] The spin–lattice relaxation time is generally recognized as the most important relaxation process. For more complete discussions of relaxation phenomena and methods for their determination, see: (a) Shaw, D. "Fourier Transform NMR Spectrscopy"; Elsevier: Amsterdam, 1976. (b) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy"; Wiley-Interscience: New York, 1980.

[9] See ref 2a for the complete standard inversion–recovery diagrams.

[10] Aside from the analytical implications, the differences in T_1 values are interesting from a stereochemical viewpoint. Within the group of phosphines and the phosphine oxides, the neomenthyl isomers show longer T_1's than do the menthyl derivatives. The difference is much greater in the neomenthyl series (Table I). On the basis of X-ray crystal structures for the four compounds,[2a] the neomenthyl oxides are more sterically hindered than the menthyl oxides. More extensive T_1 and NOE experiments with degassed samples would be required to determine the source of the differences. However, based on the quantitatively prepared but not degassed reference samples, the relative NOE effects were the same within the analytical accuracy of the measurements.

[11] See: Schaeublin, S.; Hoehener, A.; Ernst, R. R. *J. Magn. Reson.* **1974**, *13*, 196.

Primary Alcohol Oxidation with *N*-Iodosuccinimide

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Some time ago, we studied the reaction of secondary[1] and tertiary[2] alcohols with *N*-iodosuccinimide (NIS). At this time, we report the oxidation of some primary alcohols with NIS. We subjected a series of eight primary alcohols to NIS oxidation with irradiation. The identity of the products obtained supports the belief[3] that alkyl hypoiodites are formed when alcohols and NIS react, followed by homolytic decomposition of the intermediate hypoiodites.

Three of the alcohols, 1-pentanol, 1-butanol, and 3-methyl-1-butanol, give, almost exclusively, tetrahydrofuran products (Table I). The yields of tetrahydrofurans obtained by treatment of these primary alcohols with NIS are much better than when the same alcohols are oxidized with lead tetraacetate[4] or cerium(IV)[5]. Tetrahydrofuran formation is one of the pathways of decomposition available for alkyl hypoiodites, the other two being carbon–carbon bond cleavage to produce alkyl iodides and alkoxy radical disproportionation to form aldehydes. The above three primary alcohols give very small percentages of the other two product possibilities.

The formation of a tetrahydrofuran product can be illustrated by a discussion of the oxidation of 1-pentanol (**1**) with NIS (**2**). When the alcohol **1** is dissolved in benzene and mixed with **2**, high yields of 2-methyltetrahydrofuran (**3**; 92–94%) could be obtained at ambient temperatures after 3 h with irradiation. Less than 2% of 1-iodobutane and pentanal were found. The stoichiometry shown in eq 1 is supported by good yields of iodine and succinimide (**4**). If the same two chemicals in chlorobenzene are allowed to combine in the dark at ambient temperatures, less than 1% of product is found in 6 h. A fourth primary alcohol, 2-methyl-1-propanol, gives 2-iodopropane

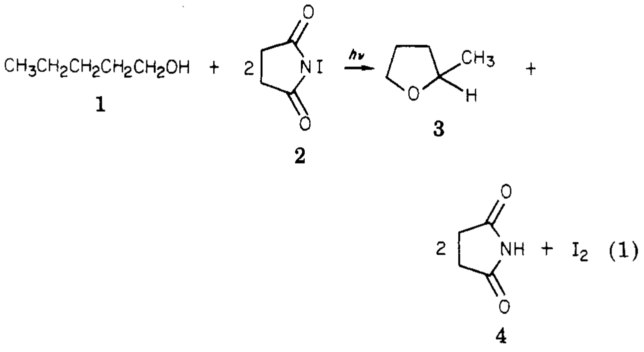

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Table I. Reactions of Primary Alcohols with Irradiation in Chlorobenzene

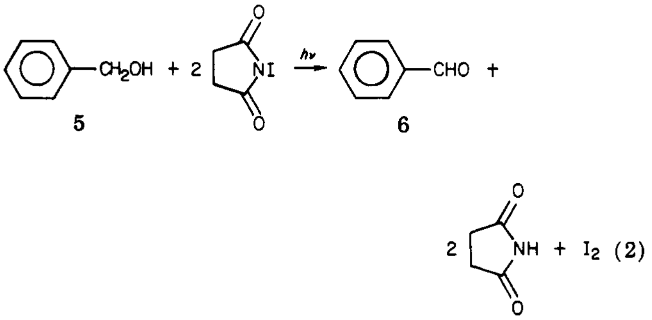
alcohols	oxidation products (% yield)	time, h	no. of runs
1-pentanol	2-methyltetrahydrofuran (92–94), 1-iodobutane (1–2), pentanal (<1)	2	3
1-butanol	tetrahydrofuran (52–61), 1-iodopropane (2–3), butanal (<1)	2	4
3-methyl-1-butanol	3-methyltetrahydrofuran (79–94), 1-iodo-2-methylpropane (2–5), 3-methylbutanal (<1)	2	5
2-methyl-1-propanol	2-iodopropane (43–51), 2-methylpropanal (5–18)	2–3	5

Table II. Oxidations of Benzyl Alcohols with Irradiation in Benzene

alcohols	oxidation products (% yield)	time, h	no. of runs
benzyl alcohol	benzaldehyde (70–90)	1–2	6
p-methylbenzyl alcohol	*p*-methylbenzaldehyde (82–93)	1–2	5
o-methylbenzyl alcohol	*o*-methylbenzaldehyde (66–84)	2–3	5
p-fluorobenzyl alcohol	*p*-fluorobenzaldehyde (87–92)	1–2	2

(43–51%), a carbon–carbon bond-cleavage product, and 2-methylpropanal (5–18%), an alkoxy radical disproportionation product as shown in Table I. The relative ease of the ejection of the isopropyl radical in the fragmentation of the isobutoxy radical intermediate is predicted by the studies of Greene[6] and Sanderson.[7]

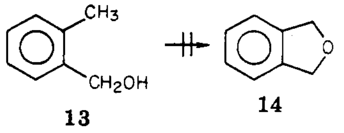
Table II outlines the oxidations of four different benzyl alcohols with NIS. The reactions were performed in benzene and good yields of the corresponding benzaldehyde products were obtained. Succinimide (84–95%) and iodine (81–96%) were found in sufficient yields to suggest the stoichiometry given in eq 2 where benzyl alcohol (**5**) is oxidized to benzaldehyde (**6**)



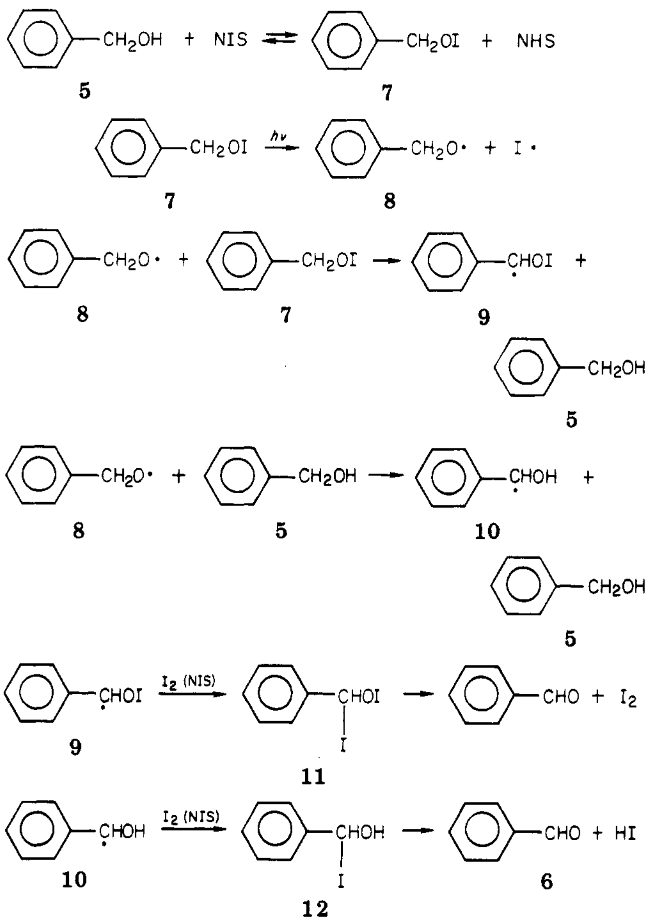
A suggested pathway for benzaldehyde formation is shown in Scheme I. The pathway outlines the accepted concept of hypoiodite **7** formation followed by homolytic cleavage of the oxygen–iodine bond by irradiation to produce the benzyloxy radical (**8**).

Once the benzyloxy radical forms it will stabilize itself, either by homolytic cleavage of its own bonds or by abstraction of a labile hydrogen atom from a neighboring molecule. The most probable reaction for the benzyloxy radical is hydrogen abstraction from the hypoiodite **7** or benzyl alcohol (**5**). Hydrogen abstraction would produce the stable oxybenzyl radicals **9** and **10**, shown in Scheme I. Reaction of either of the two radicals, **9** or **10**, with iodine (or NIS) would form the intermediates **11** and **12**, both of which would give benzaldehyde on decomposition.

It was thought that *o*–methylbenzyl alcohol (**13**) could give phthalan (**14**) as a product, but only the aldehyde was found. Phthalan and *o*-methylbenzaldehyde separated cleanly on the chromatograph. When phthalan was added to a completed reaction, the new phthalan peak appeared in the chromatograph separation.



Scheme I



All eight of the primary alcohols also were treated with NIS in the dark at ambient temperatures for 2–6 h. The alcohols in Table I gave less than 1% product yields and the benzyl alcohols in Table II gave less than 5% product yields.

Experimental Section

Analyses were performed on a Perkin-Elmer 810VPC instrument and a Varian Aerograph Model 700VPC instrument. Liquid chemicals used in the reaction mixture and standard VPC mixtures all had greater than 99.5% purity as determined by gas chromatography. The benzene was spectroscopically pure and was used without further purification. VPC analysis were done on 6 ft × 0.25 in. and 12 ft × 0.25 in. copper columns of 10% SE-30, 7% SE-30 and 3% Carbowax 20-M, and 10% Carbowax

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[6] Greene, F. D.; Savitz, M. L.; Osterholtz, F. D.; Lau, H. H.; Smith, W. N.; Zanet, P. M. *J. Org. Chem.* **1963**, *28*, 55.

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20-M. The *N*-iodosuccinimide was determined to have 96.5–99.5% active iodine and was used as purchased. Irradiation of reaction mixtures was effected with a G.E. Projector Spot 150-W, 130-V tungsten lamp.

Oxidation of 1-Pentanol with NIS and Irradiation. A 5-mL solution of 0.1065 g (1.210 mmol) of 1-pentanol in chlorobenzene was added to 0.2365 g (1.056 mmol) of NIS contained in a 10-mL flask. The condenser attached to the flask was ice-water cooled. The mixture was stirred and irradiated. Reaction times and percentage yields of 2-methyltetrahydrofuran were as follows: 20 min (15%), 40 min (58%), 60 min (80%), 80 min (91%), 100 min (93%), 120 min (94%). Trace amounts of pentanal (1%) and 1-iodobutane (<1%) were found. Material balance after 2 h was 99%. Succinimide was recovered in 83% yield and elemental iodine determination gave 0.443 mmol (84%).

Oxidation of 1-Pentanol with NIS in the Dark at Ambient Temperatures. A 5-mL solution of 0.1065 g (1.210 mmol) of 1-pentanol in chlorobenzene was added to 0.2822 g (1.254 mmol) of NIS contained in a 10-mL flask. The flask was covered with aluminum foil in a dark fume hood. The mixture was stirred. Reaction times and percentage yields of 2-methyltetrahydrofuran were as follows: 1 h (1%), 2.5 h (<1%), 10 h (<1%). Less than 1% yields were also found for pentanal and 1-iodobutane. A 99.5% recovery was made of the starting alcohol. Titration for positive iodine gave 1.264 mmol (101%).

Oxidation of *p*-Fluorobenzyl Alcohol with NIS and Irradiation. A 5-mL solution of 255 mg (2.03 mmol) of *p*-fluorobenzyl alcohol in benzene was added to 232 mg (1.03 mmol) of NIS is a 10-mL reaction flask. The mixture was stirred and irradiated. Reaction times and percentage yields of *p*-fluorobenzaldehyde were as follows: 12 min (69%), 35 min (70%), 1 h (76%), 2.5 h (87%). Succinimide was found in 84% and the iodine determination gave 83%. No bond-cleavage iodobenzene products were found.

Iodine Determination. The iodine produced in the oxidation of primary alcohols with NIS was determined by adding the reaction mixtures to 25 mL of a 1:1 mixture of acetic acid and water. Several drops of concentrated hydrochloric acid were added, and the iodine was titrated with a standardized solution of thiosulfate.

Succinimide Determination. Succinimide was recovered in two ways: by filtration of the cooled reaction mixtures to obtain the solvent insoluble succinimide or by extraction of the reaction solvents with water and evaporation of the water.

Acknowledgment. We are grateful to the Research Corp. and to the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research.

Registry No. **1**, 71-41-0; **2**, 516-12-1; **3**, 96-47-9; **5**, 100-51-6; **6**, 100-52-7; **13**, 89-95-2; 1-butanol, 71-36-3; 3-methyl-1-butanol, 123-51-3; 2-methyl-1-propanol, 78-83-1; *p*-methylbenzyl alcohol, 589-18-4; *p*-fluorobenzyl alcohol, 459-56-3; tetrahydrofuran, 109-99-9; 3-methyltetrahydrofuran, 13423-15-9; 2-iodopropane, 75-30-9; *p*-methylbenzaldehyde, 104-87-0; *o*-methylbenzaldehyde, 529-20-4; *p*-fluorobenzaldehyde, 459-57-4.

Aerosol Direct Fluorination Synthesis of Perfluoroadamantane, the Penultimate Step

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The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation.[1] The application of this process to alkanes, ethers, cycloalkanes, ketals, and ketones has been demonstrated.[1,2] We report here the extension of the process to the synthesis of perfluoroadamantane via direct fluorination of adamantane, a feat not realized by other direct fluorination methods nor by indirect fluorination methods to any significant degree.

Due to the current interest in fluorocarbons as synthetic blood substitutes,[3] the fluorination of adamantane and substituted adamantane systems has been attempted. Moore and Driscoll, employing a CoF$_3$ method involving the recycling of partially fluorinated materials through a reactor, have successfully produced perfluoro-1-methyladamantane, perfluoro-1,3-dimethyladamantane, and perfluoro-1,3,5,7-tetramethyladamantane from 1-(trifluoromethyl)adamantane, 1,3-bis(trifluoromethyl)adamantane, and 1,3-bis(trifluoromethyl)-5,7-dimethyladamantane, respectively.[4] Lagow et al. reported the successful direct fluorination of 1,3-difluoro-5,7-dimethyladamantane, 1,3-dimethyl-5,7-bis(trifluoromethyl)adamantane, and 1-adamantylamine to the perfluorinated analogues.[5]

The direct fluorination of adamantane to the perfluoro product has remained elusive however; whereas substituted adamantane systems have been successfully perfluorinated, direct fluorination of adamantane itself has previously led only to the production of 1-hydropentadecafluoroadamantane in low yields.[7] The penultimate substitution would not take place even in pure fluorine under "vigorous" conditions.[5] At the present time the only other method for the production of perfluoroadamantane, other than via the aerosol direct fluorination method presented here, appears in a recent patent application, wherein adamantane in methylcyclohexane was contacted with a CoF$_3$ bed at 275 °C to produce 1-hydropentadecafluoroadamantane and perfluoroadamantane (no yields given).[8]

Results and Discussion

The major product collected from the aerosol direct fluorination of adamantane was perfluoroadamantane; of the products collected, *F*-adamantane comprised 74.4% of the total by weight. Based on input of adamantane, the yield of *F*-adamantane was 28%. The aerosol system is dependent on the generation of a particulate aerosol which is ideally crystalline, of uniform size, and with little tendency to aggregate. If the conditions for producing the aerosol are ideal, percent yields based on throughputs and product percent distributions will differ by only a few percent; as molecules deviate from this ideality, the percent yields based on throughput fall due to physical losses within the aerosol generator and initial reaction stage (see ref 1). Due to the relatively low volatility of adamantane these losses are significant, resulting in significant amounts of unreacted adamantane settling throughout the reactor. The majority of material traversing the reactor, however, is seen to be upward of 70% perfluorinated, and it is likely that modifications to allow higher carrier flows through the reactor would result in a significant increase in the amounts of material reaching the collection point. The

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