

Reactions of Tertiary Hypohalites¹

V. BOIDO² AND O. E. EDWARDS

Biochemistry Laboratory, National Research Council of Canada, Ottawa, Canada

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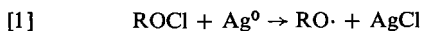
Metallic silver initiates short-chain homolytic decomposition of tertiary alkyl hypochlorites and hypobromites. Evidence is presented that the reaction of tertiary alcohols with silver oxide – mercuric oxide – bromine involves formation and homolytic decomposition of alkyl hypobromite followed by cyclization of γ -bromo alcohols. A convenient synthesis of tricyclo[4.3.1.0^{3,8}]decan-4-one (4-protoadamantanone) is described.

L'argent métallique initie la décomposition homolytique en chaîne courte d'hypochlorites et d'hypobromites d'alkyles tertiaires. On présente une preuve d'après laquelle la réaction entre les alcools tertiaires et le réactif oxyde d'argent-oxyde de mercure-brome implique la formation et la décomposition homolytique d'hypobromite d'alkyle, suivie par la cyclisation des γ -bromo alcools. On décrit une voie d'accès facile à la tricyclo [4.3.1.0^{3,8}] décanone-4 (protoadamantanone-4).

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Recent work in these laboratories has shown that the action of metallic silver on chloramides (1) and chloramines (2) produces the corresponding nitrogen radicals. Since no hydrogen chloride or chloride ions are produced, the possibility of radical chains involving chlorine atoms (3) is precluded. In addition no metallic ions are present in solution to provide complications due to oxidation–reduction processes (4). Hence this method of generating the radicals has valuable potential for the study of the reactions of nitrogen radicals in the ground state in solution.

A comparable possibility existed for the preparation of alkoxy radicals from hypohalites (eq. 1). The formation of a number of tertiary alkoxy radicals by this method



and study of their reactions is reported in this paper.

The first cases studied were those of 2-methylpent-2-yl hypochlorite (1) and hypobromite. The monomeric products characterized when 1 reacted with metallic silver at room temperature in acetonitrile are shown in eq. 2.

The γ -chloro alcohol produced could be readily cyclized to 2,2-dimethyltetrahydrofuran (2). The

ratio of hypochlorite decomposed to silver chloride formed was 4:1.

2-methylpent-2-yl hypobromite behaved similarly when treated with Tollens' silver, but the chain length was shorter.

In a reexamination of the work of Sneen and Matheny (5) we treated 2-methylpentan-2-ol with bromine, mercuric oxide, and silver oxide at 0–5 °C in pentane. The product was the corresponding hypobromite. This decomposed near room temperature into acetone, 2-pentanone, and 5-bromo-2-methylpentan-2-ol. The latter cyclized slowly at room temperature to 2,2-dimethyltetrahydrofuran (2). The cyclization was markedly accelerated by silver oxide.

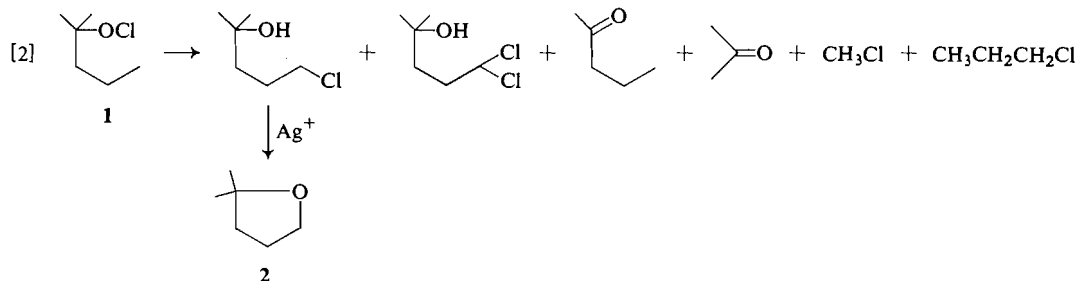
When the bromine, oxides, and alcohol reagents were mixed rapidly at room temperature in an attempt to duplicate the conditions of Sneen and Matheny, the temperature rose and reaction was complete in 10 min. No hypobromite was left, and 2,2-dimethyltetrahydrofuran had been formed. In addition acetone was shown to be present, hence the overall reaction was the same as thermal decomposition of the hypobromite followed by silver oxide induced cyclization of the γ -bromo alcohol.

As an example of a monocyclic tertiary hypohalite, 1-methylcyclopent-1-yl hypochlorite (3) was chosen for study. Cairns and Englund had shown (6) that this decomposed thermally to give a high yield of 6-chloropentan-2-one (4). Metallic silver converted 3 into 4 rapidly at room temperature. The ratio of hypochlorite converted to silver chloride produced was 9.7:1.

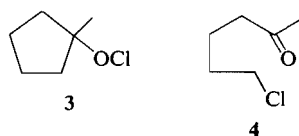
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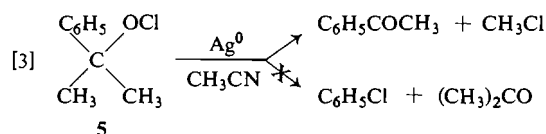
²Postdoctoral Fellow of the Consiglio Nazionale delle Ricerche (Rome), 1969–1970.



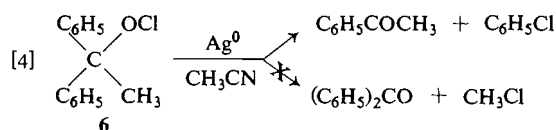
The next examples studied were 1-methyl-1-phenylethyl hypochlorite (**5**) and 1,1-diphenylethyl hypochlorite (**6**). Somewhat to our surprise



5 gave nearly exclusively fission to acetophenone (eq. 3). The ratio of ROCl/silver chloride produced was 2.4. In contrast **6** gave predominantly

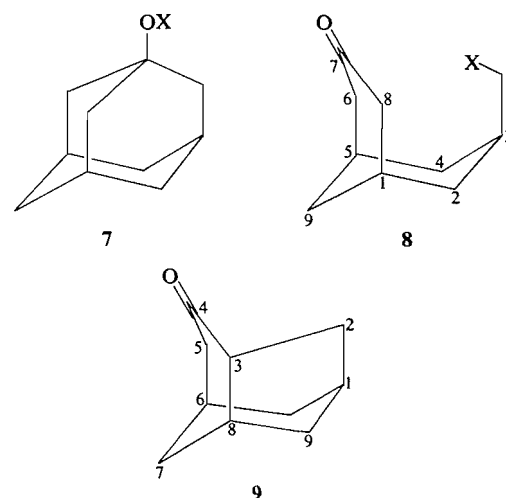


1,1-diphenylethanol, 22% of acetophenone, but no benzophenone (eq. 4). The ROCl/AgCl ratio was 1.7.



Our attention was attracted to recent syntheses (7) of tricyclo[4.3.1.0^{3,8}]decane (protoadamantane) and its derivatives. It occurred to us that 1-adamantyl hypohalites (**7**) might be converted under homolytic conditions into the corresponding 3-*endo*halobicyclo[3.3.1]nonan-7-ones (**8**), which could be cyclized to 4-protoadamantanone (**9**).

Treatment of 1-adamantyl hypochlorite in acetonitrile with Tollens' silver led to rapid reaction to give a mixture of 1-adamantanol, chlorinated adamantanols, the bicyclic ketone **8** (X = Cl), and dichloro ketones. Under the conditions chosen 4 mol of hypochlorite were decomposed for each mol of silver chloride produced. The yield of chloro ketones (calcu-

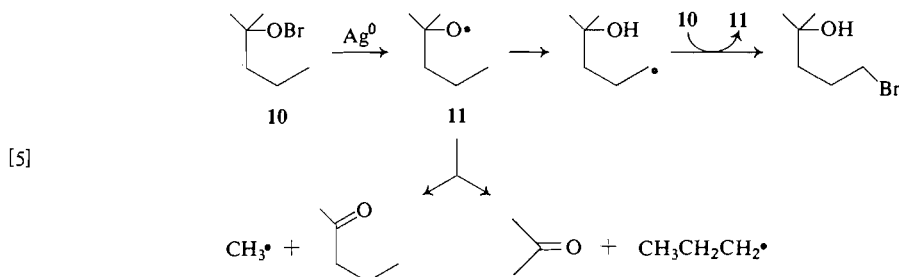


lated as **8**, X = Cl) was estimated to be 40.5%. In comparable experiments at 0° 1-adamantyl hypobromite gave an estimated 33% of bromo ketones (calculated as **8**, X = Br).

The thermal decomposition of 1-adamantyl hypochlorite was very slow in refluxing carbon tetrachloride or chlorobenzene at 110°. However it decomposed rapidly in refluxing acetonitrile. The estimated yield of chloro ketones produced was 64%. The hypobromite decomposed quite rapidly when heated in all three solvents giving approximately 63% of bromo ketones rich in **8** (X = Br).

Finally photolysis of 1-adamantyl hypochlorite in carbon tetrachloride gave a lower yield of **8** (X = Cl) than the silver initiated reaction hence was not studied in detail.

The chloro or bromo ketones **8** could be cyclized at room temperature using sodium hydride in tetrahydrofuran to give good yields (*ca.* 37% based on hypohalite used) of 4-protoadamantanone (**9**). While this work was in progress Black and Gill (8) reported the preparation of **8** (X = I) from "1-adamantyl hypoiodite",



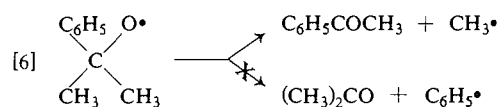
and its conversion into protoadamantanone in an overall yield of 34%. Lunn (9) has also prepared and characterized the bicyclic iodoketone (8, X = I), and described its cyclization into 4-protoadamantanone (overall yield 32%). A synthesis of 9 by deamination of 2-aminoadamantan-1-ol has recently been reported by Lenoir and Schleyer (10).

Discussion

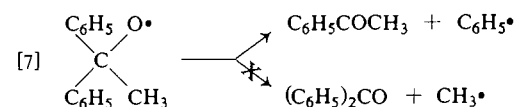
The products from the silver initiated decomposition of 2-methylpent-2-yl hypochlorite and hypobromite are exactly what would be expected for a homolytic chain reaction (eq. 5). The fact that the Sreen and Matheny (5) conditions produce hypobromites which are thermolabile, and that the products from 2-methylpent-2-yl hypobromite fit the above homolytic pattern, suggest that their postulate of reaction involving cationic oxygen is in error. It appears that the unique role of the silver oxide is to cyclize the γ -bromo alcohol. This conclusion is in harmony with those of Akhtar and co-workers (11) and Smolinsky and Feuer (12).

The cyclization of primary and secondary alcohols using the bromine-silver oxide or iodine-mercuric oxide combination recently described by Mihailovic and co-workers (13) is not inconsistent with homolytic decomposition of intermediate hypohalites. Finally, the claim by Sommer and co-workers (14) that their observed solvent effects support a cationic oxygen mechanism for the silver oxide-bromine-secondary alcohol reactions is not convincing. The addition of tetrahydrofurans, or the use of ethers as solvents was shown to eliminate an induction period and increase the yield of cyclic ethers at the expense of ketonic products. We suggest that this effect is most simply explained as initiation of homolytic decomposition of the alkyl hypobromites by peroxide in the ethers (see ref. 1).

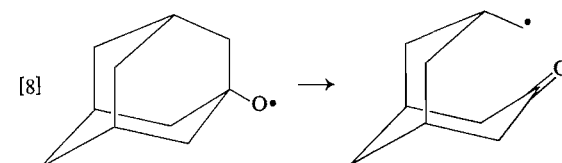
The direction of fission of 1-methyl-1-phenylethoxy radical suggests that the transition state for the decomposition resembles the products, and that the difference in energy of formation of phenyl or methyl radicals is more than offset by development of acetophenone resonance³ (eq. 6).



In the case of 1,1-diphenylethoxy radical however, the resonance energy gain in producing benzophenone is probably slightly more than that for formation of acetophenone.⁴ Hence the nearly exclusive formation of the latter and phenyl radicals (eq. 7) suggests that these radicals are at least 5 kcal/mol more stable than methyl radicals.



In view of the compactness of the adamantane skeleton, it was an open question whether or not the 1-adamantoxyl radical would undergo fission to the keto alkyl radical (eq. 8). However, the



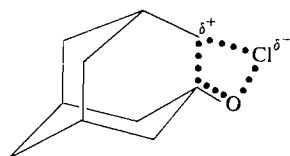
free energy of activation for the fission must be low since the reaction competes favorably with

³However there is no clear correlation with the accepted value for acetophenone resonance (only 1 kcal/mol more than benzene) (15).

⁴The resonance contribution of the benzophenone carbonyl is estimated to be zero (15) but this seems improbable.

the abstraction of hydrogen from solvent and other molecules.

Black and Gill (8) considered the thermal decomposition of 1-adamantyl hypoiodite⁵ and the other hypohalites studied to be homolytic. Our results with metallic silver prove that the adamantoxy radical does give the bicyclic ketone. However, the solvent effect on the thermal decomposition of the hypochlorite is only consistent with charge development in the transition state, which probably resembles 12. Even in



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acetonitrile, however, considerable adamantanol and chlorinated adamantanol were produced, hence a simultaneous homolytic fission of the hypochlorite was taking place. In view of the apparent absence of a solvent effect, the thermal decomposition of the hypobromite appears to be more homolytic in character. However the yield of bromoketones (*ca.* 63%), in contrast to the 33% yield for the pure homolytic process (silver initiated), suggests that a bond reorganization process is the main reaction path rather than reaction via adamantoxy radicals.

Experimental

The acetonitrile used was spectroscopic quality. The metallic silver used was a light brown solid produced by the action of formaldehyde on silver ammonium ion solution (Tollens' reagent), then thorough washing with water. It was prepared fresh for each experiment.

The g.l.c. was done on a 1/4" × 6' column of silicone rubber (10% SE30 on acid-washed silanized chromosorb W). Alumina was Woelm neutral grade, with activities according to Brockmann and Schodder (16).

Silver chloride was estimated by extraction into aqueous ammonia, filtration, reprecipitation by acid, filtration, and drying at 100°. Silver bromide was estimated by dissolving unreacted silver in nitric acid, filtration, washing, and drying. Yields and ratios are corrected for aliquots removed for titration.

Action of Silver on 2-Methyl-pent-2-yl Hypochlorite

Glacial acetic acid (10 ml) was added with stirring to an ice-cold mixture of 2.38 g of 2-methylpentan-2-ol and 150 ml of strongly alkaline 8% sodium hypochlorite

solution. After 2 h stirring at 5 °C, the mixture was extracted with pentane. The pentane solution was washed with sodium carbonate solution then dried over sodium sulfate. The solvent was removed below room temperature on a rotating evaporator leaving 2.48 g of yellow oil. Its i.r. spectrum in methylene chloride showed the presence of a small amount of parent alcohol and a ketone.

The oil was dissolved in 22.5 ml of acetonitrile and 2.5 ml of water (final volume near 27 ml). Titration of 1 ml showed the presence of 1.57 g of hypochlorite. The remaining solution was purged with a stream of nitrogen. Tollens' silver from 2.6 g of silver nitrate was then added in portions over 20 min while stirring under nitrogen. After a total reaction time of 30 min only 1% of the hypochlorite remained. This was destroyed by addition of more silver, then the suspension was filtered. The precipitate was washed with acetonitrile.

The combined filtrates were distilled through a short Vigreux column giving (a) 2 ml of fore-run and (b) 20 ml b.p. near 80° (bath up to 120°). A residue (c) of 1.3 g remained.

The fore-run (a) and a methanol solution of trimethylamine was heated in a sealed tube at 100° for 5 h. The solvent was then distilled leaving 87 mg of crystalline salt. Its n.m.r. spectrum in D₂O had signals near δ 1.0 (triplet, *J* = 7 Hz), 1.2–2.1 (broad multiplet), 3.1 (sharp singlet), and 3.3 (triplet, *J* = 7) in intensity ratios of 3:2:11:2. This corresponds to a mixture containing 85% of trimethyl propylammonium iodide and 15% of tetramethylammonium iodide.

The main distillate (b) was partially dried using sodium sulfate. To this was added 1 g of *p*-nitrophenylhydrazine and the mixture held near 75° for 1 h by which time no carbonyl absorption was left in its i.r. spectrum. The solvent was removed under reduced pressure and the residue taken up in methylene chloride. The solution was washed twice with 2 *N* sulfuric acid, then with sodium carbonate solution.

The distillate from quaternary salt formation of fore-run (a) was treated in the same way. The combined hydrazone weighed 824 mg. Its n.m.r. spectrum contained peaks at δ 1.18 (triplet, *J* = 7 Hz) and at 1.96 and 2.10 corresponding to the *p*-nitrophenylhydrazones of 2-pentanone (1.18, 1.96, and 2.10) and acetone (1.93 and 2.08).

The intensities corresponded to 55% acetone derivative and 45% 2-pentanone, with a total ketone yield of 47%.

The residue (c) was dissolved in acetonitrile and stirred at room temperature with silver oxide from 657 mg of silver nitrate for 3 h. The suspension was filtered, the filtrate diluted with an equal volume of water, and extracted with pentane. The dried pentane solution was concentrated to small volume using a Vigreux still head. The residue gave n.m.r. signals at δ 1.24 (sharp) and 3.88 (triplet, *J* = 7 Hz) corresponding to the signals from authentic 2,2-dimethyltetrahydrofuran. The i.r. spectrum of the residue had seven peaks in the fingerprint region identical with those of 2,2-dimethyltetrahydrofuran, and the mixture gave a g.l.c. peak at the same retention time as authentic ether.

In another run, the fraction corresponding to (c) was distilled over a short path under 10 mm pressure. Distillate collected at a bath temperature up to 70° was a bad mixture but that collected at 70–100° contained approximately 50% of 5-chloro-2-methylpentan-2-ol as indicated

⁵Lunn (9) points out that the hypoiodite may not be involved in the cleavage by lead tetraacetate–iodine reagent.

by n.m.r. signals at δ 0.74 (sharp) and 4.15 (triplet, $J = 6.5$ Hz).

Anal. Calcd. for $C_6H_{13}ClO$: Cl, 38.53. Found: 40.76.

This fraction and the residue gave an n.m.r. triplet at δ 5.85 ($J = 6$ Hz) corresponding to the presence of 5,5-dichloro-2-methylpentan-2-ol.

The silver chloride produced weighed 307 mg. Hence the $ROCl/AgCl$ ratio was 4.

Action of Silver on 2-Methylpent-2-yl Hypobromite

Hypobromous acid was prepared from 3.99 g of bromine in 120 ml of water at 0° using 9.3 g of silver sulfate in the dark. The solution was decanted from silver bromide and added to a solution of 2.3 g (22.5 mmol) of 2-methylpentan-2-ol in 50 ml of trichlorofluoromethane. After 15 min vigorous mixing at 0° the organic layer was separated, washed with ice-water, and dried over sodium sulfate. The solvent was removed at 0° on a rotating evaporator and the residue dissolved in 30 ml of acetonitrile. Iodimetric titration showed the presence of 15.5 mmol of hypobromite.

Tollens' silver from 4.29 g of silver nitrate was added under nitrogen to a solution of the hypobromite (15.2 mmol) in 30 ml of acetonitrile. After 0.5 h stirring at 0° under nitrogen, all the hypobromite had reacted.

The solids were removed by filtration then the bulk of the acetonitrile removed by distillation (oil bath). The residue was dissolved in ether, the ether solution washed four times with water, dried, and distilled. The brown mobile oil had an n.m.r. spectrum corresponding to 5-bromo-2-methylpentan-2-ol (221 mg, 1.22 mmol). The characteristic signals were a singlet at δ 1.31 and a triplet ($J = 6.5$ Hz) at δ 3.63 in the ratio of 3:1.

To the distilled acetonitrile was added 1.5 g of *p*-nitrophenylhydrazine and a few drops of acetic acid. The mixture was refluxed for 1 h, then the solvent removed under reduced pressure. The residue was taken up in methylene chloride. The solution was washed three times with 2 *N* sulfuric acid, with sodium carbonate solution, then with water, dried, and distilled. A crystalline residue (1.1 g) remained. Examination of its n.m.r. spectrum showed it to consist of 63% *p*-nitrophenylhydrazone of 2-pentanone (3.14 mmol) (δ 1.18 (triplet $J = 7$ Hz), 1.96, and 2.1) and 37% acetone derivative (δ 1.93 and 2.08).

The amount of silver bromide produced was 1.79 g (9.5 mmol) i.e. $ROBr/AgBr = 1.6$.

Thermal Decomposition of 2-Methylpent-2-yl Hypobromite

(1) In an attempt to duplicate the conditions of Sneed and Matheny (5) a suspension was prepared of 1.6 g of 2-methyl-2-pentanol, 5.10 g of yellow mercuric oxide, and 2.37 g of silver oxide in 30 ml of dry pentane. To the stirred mixture in dim light, 1.0 g of bromine was added. The temperature of the mixture rose to 35° due to heat of reaction. After 10 mins stirring the mixture was filtered and the salts washed with pentane. The bulk of the solvent was removed by distillation. Both the distillate (A) and residue (B) contained carbonyl compounds (i.r.). The carbonyl compound in the distillate (A) was converted to its *p*-nitrophenylhydrazone by addition of 1.4 g of *p*-nitrophenylhydrazine, 20 ml of acetonitrile, 20 ml of ethanol, and 4 drops of acetic acid, then refluxing the solution for 1 h. The solvents were removed and the derivative purified as described in the silver catalyzed reaction. It proved to be 325 mg of quite pure acetone

p-nitrophenylhydrazone (two 3H singlets at δ 1.98 and 2.13).

The residue (B) gave an i.r. band at 1050 cm^{-1} (C—O—C) and had n.m.r. signals characteristic of 2,2-dimethyltetrahydrofuran (δ 1.25 (singlet), 3.92 (triplet, $J = 6.5$ Hz)).

(2) The above reaction was repeated, except that the bromine was added slowly while the temperature was kept below 5°C . After 10 min the solution was filtered. The filtrate did not show any —OH or C=O stretching bands in the i.r., nor the characteristic C—O—C band, hence the product was apparently 2-methylpent-2-yl hypobromite.

The solution was then refluxed in the dark until colorless (15 min), at which time no hypobromite remained (iodimetry). The i.r. spectrum now showed bands at *ca.* 3200 (OH), 1720 , and a very weak band at 1056 cm^{-1} . The solution was divided into two equal parts.

From one part, the solvent was removed at 0° under 20 mm pressure. The residue contained 5-bromo-2-methylpentan-2-ol as indicated by n.m.r. signals at δ 3.53 (triplet, $J = 6.5$ Hz) and 1.28 (singlet) in the ratio 1:3 and a pair of peaks with equal intensity at *m/e* 162 and 164 ($M^+ - H_2O$) in its mass spectrum. The presence of 5,5-dibromo-2-methylpentan-2-ol was indicated by an n.m.r. triplet at δ 5.90 ($J = 6$ Hz).

To the other part was added 1.2 g of silver oxide and the mixture stirred at room temperature for 10 min. The i.r. spectrum of the solution now had bands at *ca.* 3450 cm^{-1} (weaker) while one at 1050 cm^{-1} (C—O—C) had become very strong. Stirring for 4 h effected no further marked change in the spectrum.

After filtration, the solution was passed through a column of 14 g of alumina, activity IV. The substance eluted with pentane was very volatile, some passed with the pentane when this was distilled through a short Vigreux column. The residue (312 mg) which still contained a little pentane had spectra characteristic of 2,2-dimethyltetrahydrofuran ($\nu_{\max}(\text{pentane}) 1050\text{ cm}^{-1}$; n.m.r. signals at δ 1.25 (singlet) and 3.9 (triplet, $J = 7$ Hz) in the ratio 3:1).

Action of Silver on 1-Methylcyclopentyl Hypochlorite

A solution of 2.5 g (25 mmol) of 1-methylcyclopentanol and 5.7 ml of acetic acid in 10 ml of acetonitrile was added slowly with stirring in the dark to 50 ml of ice-cold 11.6% aqueous sodium hypochlorite solution. After 45 min stirring at 0° , the mixture was diluted with cold water and extracted twice with pentane. The pentane solution was washed with 3 20 ml portions of 3% sodium bicarbonate solution then with water. The dried pentane solution contained 20.2 mmol of hypochlorite. Its i.r. spectrum showed the absence of alcohol, but a weak carbonyl band was present at 1720 cm^{-1} .

Moist Tollens' silver, freshly prepared from 3.98 g of silver nitrate, was added over 20 min under dry nitrogen in semi-darkness to a stirred solution of 14.2 mmol of the hypochlorite in 40 ml of acetonitrile. The hypochlorite was completely destroyed in less than 0.5 h (a blank run without silver showed no reaction under these conditions).

The solution was filtered. The filtrate was reduced to small volume under reduced pressure, then the residual liquid distilled over a short path under 15 mm pressure. The first fraction of 0.21 g (bath up to 70°) was a mixture of 1-methylcyclopentanol and 10-chlorohexan-2-one in the

ratio 1:5 as estimated by g.l.c. (105°; retention time 105 and 375 s, respectively). The second fraction of 1.518 g was nearly pure 6-chlorohexan-2-one (1% 1-methylcyclopentanol). The n.m.r. spectrum of the ketone had peaks at δ 1.78 (m, 4H), 2.18 (s, 3H), 2.53 (t, 2H, $J = 6.5$ Hz), 3.60 (t, 2H, $J = 6.5$ Hz). It was further characterized as its 2,4-dinitrophenylhydrazone, m.p. 80–81°, (lit. (17) m.p. 81.5°). The yield of the chloro ketone was estimated to be 1.77 g (13.2 mmol, 93%).

The silver chloride produced in the reaction weighed 0.21 g (1.47 mmol). Hence the ratio of ROCl/AgCl was approximately 9.7.

Action of Silver on 2-Phenylprop-2-yl Hypochlorite

A solution of 2.04 g of 2-phenylpropan-2-ol in 5 ml of acetonitrile was added to 50 ml of ice-cold sodium hypochlorite solution (chlorine bubbled into a solution of 9 g of sodium hydroxide in 50 ml of water until the pH reached 5). The mixture was stirred in an ice bath for 3 h then extracted with pentane. The dried pentane solution was concentrated under reduced pressure leaving a faintly yellow oil. This was dissolved in acetonitrile to make 25 ml of solution containing 13.4 mmol of hypochlorite and a trace of ketone (v_{\max} 1695 cm^{-1}).

Tollens' silver from 907 mg of silver nitrate was added to the stirred hypochlorite solution, maintained at 0–5° under nitrogen. After 0.25 h 32% of the hypochlorite had reacted; after 1 h, 53%; 2 h, 68%. The reaction was pushed to completion by addition of fresh silver. The remaining 21.5 ml of solution was filtered. To the filtrate was added 2.1 g of *p*-nitrophenylhydrazine. The mixture was maintained at ca. 80° for 1 h then the bulk of the solvent was removed under reduced pressure. The residue was taken up in methylene chloride and excess *p*-nitrophenylhydrazine removed by washing with dilute sulfuric acid, then with water. The methylene chloride was removed, and the residue boiled with hexane. The crystals were collected by filtration, giving 1.58 g, m.p. 165–175°. After two recrystallizations it had m.p. 181°. Its mixed m.p. with acetophenone *p*-nitrophenylhydrazone (184°) was 182° and their n.m.r. spectra were identical. There was no sign of acetone in the original reaction mixture (i.r.) or the *p*-nitrophenylhydrazone.

The hexane extract from the *p*-nitrophenylhydrazone contained 695 mg of oil whose n.m.r. and i.r. spectra showed it to be mainly 2-phenylpropan-2-ol.

The amount of silver chloride produced was 727 mg corresponding to an ROCl/AgCl ratio of approximately 2.4.

In a parallel run (1.2 g hypochlorite in 30 ml of acetonitrile) in which the weight ratio of hypochlorite to silver was 3.4 the reaction was very fast; 68% reacted in 0.5 h, 86% in 1 h. The chain length produced, as measured by silver chloride, was 4.5. Hence the reaction is sensitive, probably to traces of oxygen.

A blank run showed that the hypochlorite was only partially converted to ketone when left at 0° for 64 h.

Action of Silver on 1,1-Diphenylethyl Hypochlorite

A solution of 2.48 g of 1,1-diphenylethanol (12.5 mmol) in 10 ml of acetonitrile containing 2.4 ml of acetic acid was added dropwise to a stirred ice-cold 11% sodium hypochlorite solution (strongly basic) in diffuse light. The mixture was stirred at 0–5 °C for 45 min. It was then diluted with water and the product extracted into

carbon tetrachloride. This was washed twice with 3% sodium bicarbonate solution. The dried solution (MgSO_4) had no OH stretching absorption and contained 12.5 mmol of hypochlorite (iodimetry). The solvent was removed under reduced pressure at 0–5 °C and the crystalline residue dissolved in 40 ml of acetonitrile.

Tollens' silver (acetonitrile washed) from 2.85 g of silver nitrate (16.8 mmol) was added in portions during 20 min to the stirred ice-cold solution of the hypochlorite under nitrogen in semi-darkness. The extent of reaction was: 0.5 h, 74%; 1 h, 78%; 2 h, 84%; 3.5 h, 86%. The reaction was pushed to completion by adding silver from 0.47 ml of silver nitrate, then the suspension was filtered. The g.l.c. examination of the filtrate showed the major products to be 1,1-diphenylethanol, acetophenone, and chlorobenzene. The solvent was removed under reduced pressure at 5 °C. The crystalline solid was recovered by filtration using pentane for washing. It proved to be 508 mg of 1,1-diphenylethanol. The pentane filtrate was passed through a column of 50 g of alumina, activity II. Forty-five milliliters of benzene eluate left an oil on evaporation at 0°. The g.l.c. showed the presence of chlorobenzene, acetophenone, and 1,1-diphenylethanol. Its n.m.r. spectrum had signals corresponding to the methyl groups of acetophenone (δ 2.5) and 1,1-diphenylethanol (δ 1.92) and to the presence of a trace of ω -chloroacetophenone (δ 4.6).

A second 45 ml of benzene eluted 0.417 g of 1,1-diphenylethanol, and 100 ml of benzene containing 5% of methanol eluted a further 0.55 of this carbinol.

The oil from the first benzene eluate was dissolved in 20 ml of ethanol containing 1 g of *p*-nitrophenylhydrazine. The solution was refluxed for 45 min then the solvent removed under reduced pressure. The residue was dissolved in methylene chloride. The solution was washed twice with 2 *N* sulfuric acid then four times with water. The dried solution was distilled, and the crystalline residue extracted repeatedly with boiling hexane. The insoluble material had m.p. 178–181° and mixed m.p. with acetophenone *p*-nitrophenylhydrazone 180–184°; yield 0.52 g (2.04 mmol). The hexane extracts yielded 0.138 g of 1,1-diphenylethanol.

The yield of once-recrystallized 1,1-diphenylethanol, m.p. 80–81°, was 1.29 g (6.5 mmol).

The amount of silver chloride produced in the reaction was 1.062 g (7.4 mmol). The ROCl/AgCl ratio was 1.7.

The yield of acetophenone, corrected for aliquots removed, was 22%. No benzophenone was detected among the products.

1-Adamantyl Hypobromite

Hypobromous acid was prepared from 1.05 g of bromine and 2.18 g of silver sulfate in 30 ml of water at 0–5 °C in semi-darkness. A solution of 765 mg of 1-adamantanol in 10 ml of methylene chloride was added and the mixture stirred in an ice bath. More solid silver sulfate was added at intervals during 1 h of stirring. The light brown organic layer was separated and the aqueous layer washed with more methylene chloride. Evaporation of the methylene chloride under reduced pressure left a pale brown crystalline residue. Iodimetry showed this to contain 4.2×10^{-3} mol of hypobromite (84%).

Action of Silver on 1-Adamantyl Hypobromite

A solution of 4.2×10^{-3} mol of hypobromite in 15 ml

of acetonitrile was prepared. Its i.r. spectrum showed that only a trace of carbonyl compounds were present.

The solution was purged with nitrogen, then Tollens' silver from 1.25 g of silver nitrate (washed with acetonitrile) was added. After 0.5 h stirring at 0° under nitrogen, 98.5% of the hypobromite had reacted. After a further half hour of stirring the mixture was filtered and the solid washed with acetonitrile. The filtrate was taken to near dryness below room temperature under reduced pressure. The residue was dissolved in methylene chloride, then the solution washed with water, dried, and the solvent evaporated. The residue was adsorbed from benzene onto 17.5 g of silica gel. Benzene-methylene chloride mixture and methylene chloride eluted ketonic material and finally mixtures of ketone and alcohol. The total yield of ketone produced was estimated to be 33% (monobromo ketone). This was cyclized using excess sodium hydride in tetrahydrofuran at room temperature during 18 h. The product was passed in pentane solution through a column of 1 g of alumina, activity II. The pentane eluate was sublimed at temperatures up to 190°, 1 atm giving 136 mg of fairly pure protoadamantanone (9). Its identity was confirmed by t.l.c. and i.r. spectrum in comparison with authentic material. The precipitate contained 100 mg of nearly pure 1-adamantan-1-ol which was removed by a chloroform wash.

The silver bromide produced weighed 413 mg. The ratio of hypobromite reacted to silver bromide was 1.9.

Thermal Decomposition of 1-Adamantyl Hypobromite

A solution of 3.0 mmol of the hypobromite in 25 ml of acetonitrile was refluxed in semi-darkness under nitrogen. Decomposition was complete in 0.5 h. The solvent was removed under reduced pressure, leaving a residue of 940 mg whose i.r. spectrum showed the presence of hydroxyl and carbonyl groups. It was extracted twice with hot pentane. The pentane insoluble fraction (180 mg) contained 20.4% bromine, and appeared to be a mixture of brominated adamantanol.

The pentane-soluble products were adsorbed from methylene chloride onto 14 g of silica gel. Eluates (15 ml each) 1 and 2 gave 127 mg whose n.m.r. and i.r. spectrum showed it to be 3-bromomethylbicyclo[3.3.1]nonan-7-one (8, X = Br) and a component with ν_{\max} 1730 cm^{-1} and extra n.m.r. signals at δ 4.18 (doublet) and 4.9 (doublet). Eluates 3-10 (325 mg) were nearly pure 8 (X = Br). Eluates 11-15 (methylene chloride-ether) contained some ketone but were rich in alcohols. Their bromine content was only 6.6%. The total yield of ketonic product (calculated as 8 (X = Br)) was 63% based on original hypobromite.

After removal of an analytic sample, fractions 3-10 were cyclized using sodium hydride (see preparation of protoadamantanone), giving 180 mg of sublimed crystalline product. By g.l.c. this contained 90% of protoadamantanone. The total possible yield of protoadamantanone was estimated to be 40%.

The decomposition of 1-adamantyl hypobromite in refluxing carbon tetrachloride was fast (0.5 h). The ratio of carbonyl absorption to CH stretching absorption in the i.r. spectrum of the total product showed the yield of 8 to be comparable to that in the thermal decomposition in acetonitrile.

3-Bromomethylbicyclo[3.3.1]nonan-7-one (8, X = Br)

After recrystallization from pentane this formed plates, m.p. 62-63°. It had $\nu_{\max}(\text{CHCl}_3)$ 1705 cm^{-1} and n.m.r. signals at δ 3.23 (2H, doublet, $J = 6.5$ Hz), 2.75 to 1.5 (11H, multiplet), and 0.98 (2H, broad signal).

Anal. Calcd. for $\text{C}_{10}\text{H}_{15}\text{BrO}$: C, 51.97; H, 6.54; Br, 34.57. Found: C, 51.87; H, 6.47; Br, 34.90.

Tricyclo[4.3.1.0^{3,8}]decan-4-one (4-Protoadamantanone)

To a solution of 88 mg of 3-bromomethylbicyclo[3.3.1]nonan-7-one in 5 ml of anhydrous tetrahydrofuran was added 50 mg of a 50% dispersion of sodium hydride in oil. The mixture was stirred overnight while protected from moisture and carbon dioxide. The suspension was filtered through Celite, and the solid washed with pentane. The residue after removal of the pentane was sublimed at 35-40° under 10^{-2} mm. The 53 mg of crystalline sublimate had m.p. 205-208° (sealed capillary). After removal of two minor impurities by t.l.c., recrystallization from pentane, and resublimation, it had m.p. 208-210°. It gave a parent ion with m/e 150, $\nu_{\max}(\text{CHCl}_3)$ 1705 cm^{-1} and an n.m.r. signal at δ 2.72 (approximately 2H) probably arising from the proton on C-3 and the equatorial proton on C-5.

Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}$: C, 79.95; H, 9.39. Found: C, 79.78; H, 9.22.

1-Adamantyl Hypochlorite

1-Adamantan-1-ol (810 mg, 5.33 mmol) was dissolved in 10 ml of acetonitrile and 4 ml of acetic acid. The solution was added dropwise to 40 ml of a stirred ice-cold 11% solution of sodium hypochlorite in water (strongly alkaline) over the course of 15 min. The mixture was stirred vigorously at 0° in diffuse light for 1 h. The product was extracted into pentane and the pentane solution washed with water then twice with 3% sodium bicarbonate solution. After drying the pentane was evaporated, leaving a white solid. This was dissolved in 20 ml of acetonitrile. Its i.r. spectrum showed the presence of only a trace of carbonyl compound, but the carbonyl peak grew steadily in intensity in the i.r. beam. Iodimetry showed the presence of 4.84×10^{-3} mol (91%) of hypochlorite.

Action of Silver on 1-Adamantyl Hypochlorite

A solution of 4.8 mmol of the hypochlorite in 20 ml of acetonitrile was purged with nitrogen. Tollens' silver from 1.5 g of silver nitrate (washed with acetonitrile) was added and the mixture stirred under nitrogen in an ice bath. After 0.5 h no hypochlorite was left. The solids were removed by filtration and the solvent removed nearly completely under reduced pressure below room temperature. The residue was taken up in methylene chloride then the solution washed with water, dried, and distilled. The products were adsorbed from benzene onto 25 g of silica gel. Benzene-methylene chloride (1:1) eluted 329 mg of colorless oil which was the chloroketone 8 (X = Cl) contaminated with dichloroketone.

Anal. Calcd. for $\text{C}_{10}\text{H}_{15}\text{ClO}$: Cl, 18.99. Found: Cl, 23.4.

Methylene chloride eluted 44 mg of the chloroketone containing some alcohols. The total yield of chloroketones (calculated as 8) was estimated to be 1.86 mmol (40.5%). Methanol in chloroform eluted 521 mg of crystalline alcohols. The chlorine content (12.7%) cor-

responded to 67% of monochloroadamantanol in the mixture.

The yield of silver chloride (1.14 mmol) corresponded to a hypochlorite to silver chloride ratio of 4.

Thermal Decomposition of 1-Adamantyl Hypochlorite

(a) In Acetonitrile

A solution containing 3.36 mmol of the hypochlorite and 250 mg of adamantanol in 25 ml of acetonitrile was refluxed in dim light under nitrogen. After 0.5 h, 70% had reacted; 1.5 h, 83%; 2 h, 87%. The reaction was complete in 4 h. The solvent was removed under reduced pressure and the residue adsorbed from benzene onto 16 g of silica gel. The benzene eluates (50 ml) gave 66 mg of oil with $\nu_{\max}(\text{CH}_2\text{Cl}_2)$ 1730 cm^{-1} and containing 37.3% chlorine. Methylene chloride eluted 381 mg of oil with ν_{\max} 1705 cm^{-1} and an n.m.r. spectrum coincident with that of 3-chloromethylbicyclo[3.3.1]nonan-7-one. Further methylene chloride eluates (61 mg) were partly crystalline and contained considerable alcohol as well as the chloro ketone. The monochloroketone yield was estimated to be 64% based on starting hypochlorite. Methanol eluted 320 mg of crystalline alcohols containing 16.1% chlorine.

(b) In Carbon Tetrachloride

A solution of 3.9 mmol of the hypochlorite in 40 ml of carbon tetrachloride was refluxed under nitrogen. Decomposition was complete in 24 h.

(c) In Chlorobenzene

A solution of 2.94 mmol of the hypochlorite in 25 ml of chlorobenzene was heated at 110° under nitrogen. Decomposition was complete in 20 h. The products from both (b) and (c) after removal of solvents under reduced pressure gave i.r. spectra in methylene chloride with ν_{\max} 3600, 3420, and 1715 cm^{-1} . The relative intensity of the peaks was comparable to that for the crude product from the silver-initiated decomposition of the hypochlorite.

Photochemical Decomposition of 1-Adamantyl Hypochlorite

Nitrogen was bubbled for a few minutes through a solution of 2.3 mmol of the hypochlorite in 35 ml of carbon tetrachloride at 0 °C. The solution was then irradiated with light from a 100 W Hanovia high pressure mercury lamp filtered by a Corax sleeve. Decomposition was complete in less than 0.5 h. The solution now had i.r. absorption at 3600, 3370, and 1725 cm^{-1} . The intensity of the carbonyl absorption relative to the CH stretching absorption was less than that in the thermal or silver-initiated reactions in acetonitrile.

Comparable results were obtained when the hypochlorite was photolyzed at -10° in trichlorofluoromethane.

3-Chloromethylbicyclo[3.3.1]nonan-7-one

The colorless oil from thermal decomposition of 7 (X = Cl) was distilled over a short path under 10^{-2} mm at a bath temperature of 60°. It had $\nu_{\max}(\text{CH}_2\text{Cl}_2)$ 1705 cm^{-1} and gave n.m.r. signals at δ 3.35 (2H doublet), 2.18–1.6 (11H mult.), and a broad 2H signal centered at δ 1.10.

Anal. Calcd. for $\text{C}_{10}\text{H}_{15}\text{ClO}$ (mol. ion m/e 186): C, 64.33, H, 8.10; Cl, 18.99. Found (186): C, 64.11; H, 7.92; Cl, 19.18.

The chloro ketone cyclized smoothly when treated with sodium hydride in tetrahydrofuran at room temperature (see cyclization of the bromo ketone). From 350 mg of the crude chloro ketone from the thermal reaction 186 mg of crude 4-protoadamantanone was obtained. The g.l.c. showed this to be over 90% pure. The contaminant was a chloro ketone as shown by analysis (1.4% chlorine).

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