Reaction of 10 with Methyl Vinyl Ketone. To a solution consisting of 0.13 ml of water, 0.13 ml of acetic acid, and 62 mg of sodium acetate was added 0.100 ml of methyl vinyl ketone and 215 mg (1.11 mmol) of 10 in 1 ml of benzene. The mixture was refluxed under nitrogen for 4 hr, cooled, diluted with benzene, and extracted with 5% HCl. The organic phase was washed successively with water, 10% NaHCO$_3$, and brine, dried (Na$_2$SO$_4$), and evaporated in vacuo to give 179 mg of a yellow oil. GLC analysis of (5-ft 4% QF-1, 175°) of this oil showed 14 and 15 in a ratio of about 1:5 by comparison of the retention times with those of authentic samples.

Reaction of 11 with Methyl Vinyl Ketone. To the same aqueous acetic acid solution used above was added 0.070 ml of methyl vinyl ketone and 193 mg (1.0 mmol) of 11 in 1 ml of benzene. The mixture was refluxed for 4.5 hr and worked up as above to give 142 mg of a yellow oil. GLC analysis of this oil showed 14 and 15 in a ratio of about 1:5, and a small amount of a third component which was isolated by preparative GLC (10-ft 4% QF-1, 190°) and tentatively identified as the trione 13 by its ir [(CCl$_4$) 1695, 1720 cm^{-1}] and mass spectra (mol wt 210).

Registry No.—2 (R = H), 78-94-4; 4 (R = H), 42576-97-6; 5, 53940-63-9; 10, 53940-64-0; 11, 53940-65-1; 12, 20990-14-1; cis-14, 53940-66-2; trans-14, 53940-67-3; 15, 53940-68-4; 16, 53940-69-5; 17, 53940-70-8; pyrrolidine, 123-75-1; carbon tetrabromide, 558-13-4.

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A Novel Chlorination of the Adamantyl System by Silver Salts in Carbon Tetrachloride

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Silver acetate reacts with 1-bromoadamantane in carbon tetrachloride to produce 3-chloro-1-adamantyl acetate as the major product. Silver bromide acts on adamantane in CCl$_4$ to give a low yield of 1-chloroadamantane. Bromine, phosgene, bromotrichloromethane, and hydrogen chloride are significant by-products. Addition of silver acetate to the silver bromide greatly increases the yield of chlorinated adamantanes. Similar treatment of 1-adamantyl acetate with these same silver salts in CCl$_4$ gives mainly 3-chloro-1-adamantyl acetate. Silver bromide is the primary initiator of these free-radical chlorinations but, unlike many radical processes, oxygen is a requirement for its propagation. Catalysis by silver acetate was traced to the intermediacy of bromine chloride which can function as an efficient initiator for the carbon tetrachloride chlorination of adamantane.

In connection with concurrent studies in the field of adamantane chemistry, we needed an authentic sample of 1-adamantyl acetate. Although we were aware of its synthesis[2] from the alcohol by treatment with acetic anhydride, production of the acetate from 1-bromoadamantane and silver acetate in carbon tetrachloride appeared to be a feasible alternative to that procedure.

It was observed, however, that after refluxing for 20 hr and standing for 4 days, the principal product was 3-chloro-1-adamantyl acetate (2) with the anticipated 1-adamantyl acetate (3) forming in considerably smaller amounts (eq 1).

In addition to typical acetate absorptions at 1740 and 1240 cm^{-1} the infrared spectrum of chloroacetate 2 showed a band at 840 cm^{-1} attributable to C–Cl stretching. An nmr spectrum displayed five peaks at τ 7.63, 7.74, 7.93, 8.10, and 8.40 corresponding to 2, 2, 8, 3, and 2 protons, respectively. Structure 2 was further confirmed by a spontaneous positive test toward alcoholic silver nitrate reagent.

Since 1-adamantyl acetate was identified as a product, attention focused on silver acetate or the silver bromide by-product as species which might be involved in the conversion of acetate 3 to the chloroacetate 2.

A review of the literature did not reveal examples of the direct halogenation of a hydrocarbon by silver acetate initiation in CCl$_4$. In fact, the tendency for silver acetate to ho-
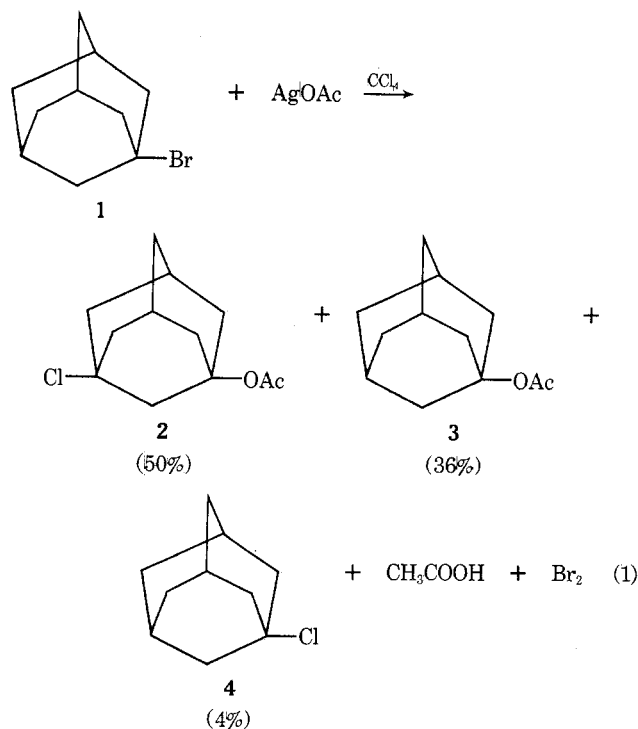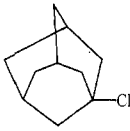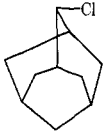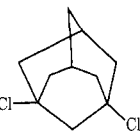

1

2
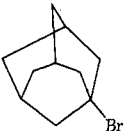(50%)

3
(36%)

4
(4%)

$$+ \ CH_3COOH \ + \ Br_2 \quad (1)$$

Table I
Products from the Carbon Tetrachloride Chlorination of Adamantane
in the Presence of Silver Salt and Halogen Initiators

		% yields of adamantyl products[a]			
Initiator	Conditions	[e]	[f]	[g]	[h]
AgBr[b]	24 hr, 77°; 72 hr, 23°	11	0	0	0
AgBr,[c] AgOAc[d]	24 hr, 77°; 72 hr, 23°	54	9	22	Trace
Br_2	6 days, 23°	40	0	21	2
BrCl	23 hr addition	36	7	22	2
BrCl–AgOAc	26 hr, 23°	46	4	16	Trace
$Br_2 + h\nu$[j]		8	0.5		15 + 2-AdBr[i] (12%)
Benzoyl peroxide[j]		22	3.3		
Di-*tert*-butyl peroxide[j]		43	6		

[a] Based on adamantane. [b] Registry no., 7785-23-1. [c] Reference 7. [d] Registry no., 563-63-3. [e] Registry no., 935-56-8. [f] Registry no., 7346-41-0. [g] Registry no., 16104-50-0. [h] Registry no., 768-90-1. [i] Registry no., 7314-85-4. [j] Reference 11b.

molyze is quite low, since pyrolysis at 400° leads to a 93% yield of acetic anhydride and silver oxide, with the homolysis product, ethane, being detected in a yield of only 1%.[3]

Although the organic chemistry of silver bromide is more obscure than that of the acetate, some examples in which this compound functions as a reagent in a redox or free radical-like capacity can be found.[4–6] A program of research was instituted to study chlorination of adamantane in carbon tetrachloride in the presence of silver acetate and/or silver bromide.

Results and Discussion

Results of reactions of adamantane with silver acetate or silver bromide in carbon tetrachloride are summarized in Chart I. Refluxing a CCl_4 solution of 1-bromoadamantane with silver acetate for 20 hr produces 1-adamantyl acetate as the sole product. Refluxing a carbon tetrachloride solution of adamantane with silver acetate for 20 hr followed by 3 days at room temperature gives only unchanged adaman-

Chart I
Reactions of Adamantane with Silver Acetate or
Silver Bromide in Carbon Tetrachloride

$$\text{AdH} + \text{AgOAc} + \text{CCl}_4 \xrightarrow[\substack{2.\ 3\ \text{days at} \\ \text{room temp}}]{1.\ \text{reflex 20 hr}} \text{no reaction}$$

$$\text{AdH} + \text{AgBr} + \text{CCl}_4 \xrightarrow[\substack{2.\ 3\ \text{days at} \\ \text{room temp}}]{1.\ 24\ \text{hr reflex}} \begin{array}{c} \text{AdCl} \\ (11\%) \end{array} \quad (2)$$

$$\text{AdH} + \text{AgBr} + \text{CCl}_4 \xrightarrow[\text{room temp}]{11\ \text{days}}$$
$$\underset{(31\%)}{\text{AdCl}} + \underset{(13\%)}{\text{BrCCl}_3} + \text{HCl} + \text{Br}_2 + \underset{(17\%)}{\text{Cl}_2\text{C}=\text{O}} \quad (3)$$

$$\text{AdH} + \text{AgBr} + \text{CCl}_4 \xrightarrow[140°]{48\ \text{hr}} \text{AdCl}(10\%) \quad (4)$$

$$\text{AdH} + \text{AgBr} + \text{CCl}_4 \xrightarrow[20\ \text{hr}]{h\nu} \text{AdCl}(8\%) \quad (5)$$

$$\text{AgBr} + \text{CCl}_4 \xrightarrow{\quad} \text{BrCCl}_3 + \text{Br}_2$$

$$\text{AdH} + \text{CCl}_4 \longrightarrow \text{no reaction}$$

Ad =

tane. Similar treatment of adamantane with silver bromide does give rise to an 11% yield of 1-chloroadamantane (4). An 11% yield of the chloride 4 was produced with 3 days of standing at room temperature, and an additional 8 days caused the yield of 1-chloroadamantane to increase to 31%. In general it was found advantageous to allow time for yields to accrue to values of about 30 in order that important by-products such as bromotrichloromethane, bromine, and hydrogen chloride be identified with greater reliability. Attempts to increase the yields through high temperature or photolysis of reaction mixtures were ineffective.

The reactions described here are routinely conducted without precaution to exclude oxygen, but when such a reaction is carried out under nitrogen atmosphere, chlorination products can be observed in yields of less than 1%, while chloroform and bromine cannot be detected. Deliberate exposure of such a reaction mixture to atmospheric oxygen causes a gradual appearance of bromine and eventually the yields of all products attain their normal values. Oxygenated adamantyl products, however, could not be detected.

Products and yields of the carbon tetrachloride chlorination of adamantane are summarized in Table I. While silver bromide can initiate chlorination of adamantane, the presence of an equivalent quantity of silver acetate increeaed the yield of the chloroadamantanes to as much as 90%.

Like adamantane, 1-adamantyl acetate underwent chlorination by treatment with silver bromide and silver acetate in CCl_4. After 1 day of refluxing and another standing at room temperature a 38% yield of chloroacetate 2 was realized; after an additional 10 days, this figure rose to 62% (eq 6).

The quality or age of silver bromide affected the yield of the chloro compounds.[7] Optimum results were achieved with freshly prepared material, and consistent results were obtained when the salt was generated in situ.

Product ratios and yields of by-products from the carbon tetrachloride chlorination of adamantane in the presence of various silver salt and halogen initiators are summarized in Table II.

Evidence for Free-Radical Chlorination by the Carbon Tetrachloride Solvent. Isolation of 2-chloroadamantane, chloroform, and bromotrichloromethane suggests a free-radical chlorination of the adamantyl nucleus by the solvent. Adamantane reactions which proceed via ionic intermediates give substitution at the bridgehead positions almost exclusively.[8] Chloroform and bromotrichloro-
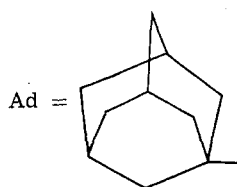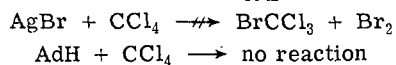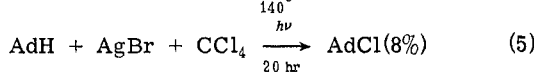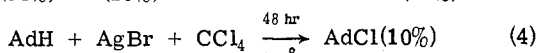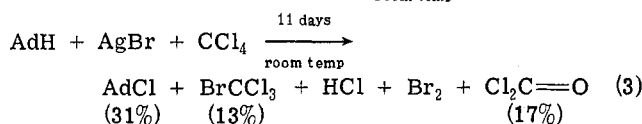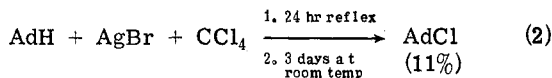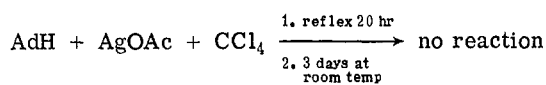
Table II
Product Ratios and Yields of By-Products Produced from the Carbon Tetrachloride Chlorination of Adamantane in the Presence of Various Silver Salt and Halogen Initiators

Initiator	Conditions	Total yield adamantyl products, %	1-Chloro-adamantane[a] / 2-Chloro-adamantane	Absolute yields, %			
				$BrCCl_3$[b]	$CHCl_3$[b]	CH_3COOH[c]	$Cl_2C=O$[b]
AgBr	10 days, 23°	31	7.6	13	0		17
AgBr–AgOAc	24 hr, 77° ; 4 days, 23°	72	5.2			66	
AgBr–AgOAc[d]	24 hr, 77°; 7 days, 23°	85	5.4	7	33	78	9
AgBr–AgOAc	72 hr, 77°	95	9.4			10	
Br_2	6 days, 23°	95	∞	8	0		0
BrCl	8 hr addition, 23°	81	5.4	30	0		0
BrCl	24 hr addition, 23°	92	5.1	10	0		0
BrCl–AgOAc	8 hr addition, 23°	81	11.0	18	0	101	0

[a] Based on GLC peak areas. [b] Based on adamantane. [c] Based on silver acetate. [d] Same as above with an additional 3 days at 23°.


3

2
(62%)

3
(36%)

+ CH₃COOH (6)

4
(5%)
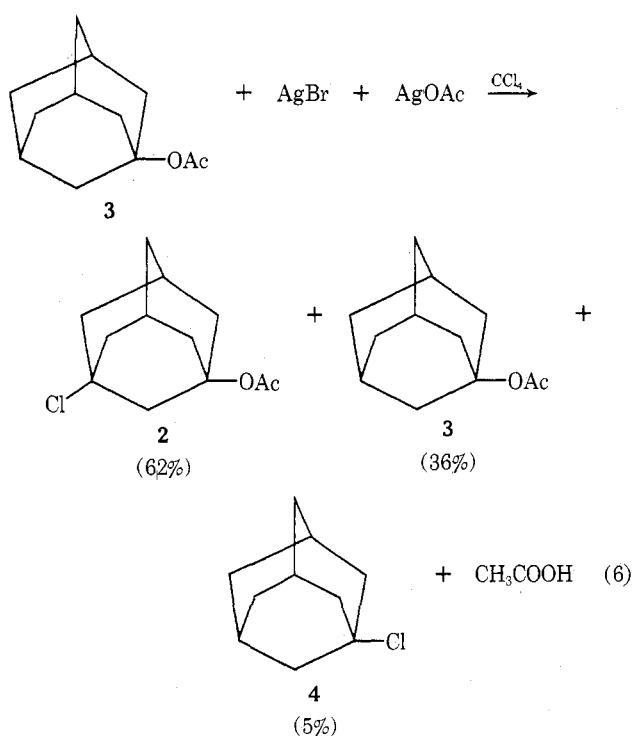
methane both can be regarded as trapped manifestations of trichloromethyl radicals, produced when the adamantyl radical abstracts chlorine from CCl_4. For more complex reasons chloroform does not always accompany free-radical CCl_4 chlorinations of adamantane, but in the thermal decomposition of *tert*-butyladamantane percarboxylate, Razuvajev[9,10] did observe, in addition to extensive chlorination of the adamantyl system, production of substantial quantities of chloroform. Owing to the low selectivity of the 1-adamantyl radical, free-radical reactions of adamantane which are initiated in CCl_4 often yield predominantly 1-chloroadamantane, even in the presence of other highly reactive halogenating agents such as bromine and NBS[11] (also see Table I). Furthermore, in the course of our investigations 1-:2-chloroadamantane ratios of 5–10 were obtained from various experiments. Such values fall comfortably within the range of what one would consider diagnostic of a free-radical process, especially when compared with other known radically initiated CCl_4 chlorinations of adamantane[11a–c] (Tables I and II).

Since bromine[12] was produced in the chlorination reactions, bromine-initiated carbon tetrachloride chlorination of adamantane was investigated. Although the reaction re-

quired 6 days for completion there was, nevertheless, a total dissipation of the bromine color. The results derived from this reaction somewhat parallel the silver bromide initiated reaction (see Tables I and II) in that scavenging of the trichloromethyl radical by bromine preferentially leads to the formation of bromotrichloromethane. In both reactions chloroform could not be detected,[13] but by comparing the yields of adamantyl products it appears unlikely that the sole hydrogen abstractors in the silver bromide reaction could have been bromine, since the 1-:2-chloroadamantane ratios differ so greatly for the two reactions.

Silver Acetate Catalysis. Chlorination of Adamantane Initiated by Bromine Chloride and Acetyl Hypobromite. For the silver bromide initiated chlorination reaction of adamantane as catalyzed by silver acetate, we propose a mechanism which is depicted in Chart II. We believe

Chart II
Proposed Mechanism for the Silver Bromide Initiated Chlorination of Adamantane in CCl_4 as Catalyzed by Silver Acetate
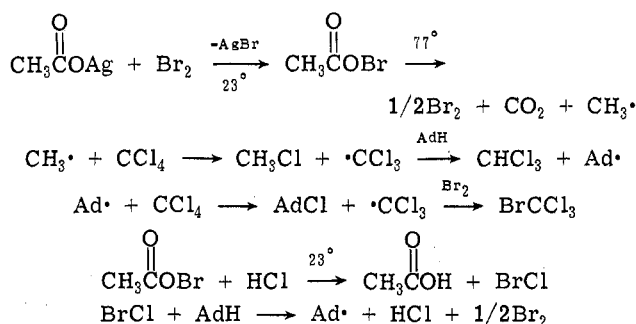
that bromine, produced as a result of the silver bromide chlorination process, is responsible for the catalytic activity of silver acetate. Bromine reacts rapidly with silver acetate, producing acetyl hypobromite.[14] Acetyl hypobromite, in the presence of HCl, would be expected to yield acetic acid and the interhalogen molecule, bromine chloride. Formation of halogens from acyl hypohalites and hydrohalic acids[15] has been known for some time and more recently Bunce and Tanner[16] showed that molecular chlorine is generated from benzoyl hypochlorite and hydrogen chloride. Thus, the bromine is converted to the highly efficient initiator, bromine chloride. Speier[17] demonstrated that bromine chloride, via hydrogen chloride formation, functions as a potent reagent for the halogenation of various types of

aliphatic hydrocarbons. In this study bromine chloride effectively halogenated cyclohexane under conditions for which bromine was unable to foster any such reaction.

In support of the above mechanism, we found that bromine chloride reacted with adamantane in CCl4 to produce good yields of chloroadamantanes in addition to bromotrichloromethane and hydrogen chloride (Tables I and II). Approximately 20 min is required for the adamantane solution to discolor a portion of bromine chloride as opposed to the 6 days required for complete discoloration of bromine. Also, the 1-chloroadamantane:2-chloroadamantane ratio derived from this reaction is the same as that derived from the silver acetate–silver bromide chlorination (Table II) and shows that bromine chloride is possibly the major hydrogen-abstracting species in the latter case as well. The interpretation of the 1-:2-chloroadamantane ratio may be somewhat clouded by the conversion of 4 to 1,3-dichloroadamantane, but an inspection of Table II reveals that even as the total yield of the AgBr–AgOAc reaction was increased by 13% this ratio increased by only 0.2%. Production of disproportionately larger yields of 1,3-dichloroadamantane from the BrCl reaction may only reflect a larger concentration of the reagent in that case.

Further evidence in support of the intermediacy of acetyl hypobromite comes from the experimental verification of acetic acid, which according to Chart II is a necessary counterpart to bromine chloride formation. Bunce and Tanner[16] reported a 60% yield for the chlorination of 2,3-dimethylbutane by benzoyl hypochlorite. By a product ratio determination these workers demonstrated that chlorine, produced from the action of hydrogen chloride on the hypochlorite, was responsible for the hydrogen abstraction processes and their sequence was further substantiated by the identification of benzoic acid.

In the silver acetate–silver bromide initiated chlorination of adamantane, acetic acid is isolated in 80% yields when the reaction is run at ambient temperatures, but only in 10% yield when the reaction is carried out at the CCl4 reflux temperature. Such a trend reflects the more rapid decomposition of the acetyl hypohalite at the higher temperature and it is conceivable that decomposition may be of sufficient rapidity so as to preclude attack by hydrogen chloride.

The reactivity trend being described here for acetyl hypobromite parallels that of benzoyl hypochlorite, which gave in benzene a moderate yield of phenyl benzoate at 3° but little at reflux.[18]

Since acetic acid and bromine chloride should be produced in equimolar quantities (Chart II), lower acetic acid yields reflect lower bromine chloride production and hence at elevated temperatures the major part of the propagation effort would have to be effected by the acetyl hypobromite decomposition products and the trichloromethyl radicals. Propagation by these less potent and thus more discriminating hydrogen abstractors,[19] as expected, causes an increase in the 1-:2-chloroadamantane ratio (Table II).

It was possible to identify methyl chloride, and though the yields of this product were not rigorously quantified, they increased notably at the higher reaction temperature. It is also significant that, whereas chloroform could not be identified in those reactions initiated merely by silver bromide, it has been detected in the silver acetate catalyzed chlorinations (Table II). This data can be rationalized by assuming that the bromine produced from the preliminary silver bromide interactions is rapidly consumed by AgOAc as soon as it is formed, and therefore is not available for scavenging of trichloromethyl radicals.

The significantly higher 1-:2-chloroadamantane ratio for

the bromine chloride chlorination carried out in the presence of silver acetate (Table II) indicates that in this case the halogen is being converted to less potent hydrogen abstractors before it attacks adamantane.

Experimental Section[20]

Silver Bromide. An aqueous solution of sodium bromide was added with stirring and exclusion of light to an equivalent quantity of a silver nitrate solution. The resulting yellow precipitate was permitted to digest for 0.5 hr, isolated by filtration, and then successively washed with water, methanol, and acetone. Drying of the product was accomplished at 0.03 nm and room temperature.

General Analytical Procedures. Reaction of Adamantane with Silver Bromide and Silver Acetate in Carbon Tetrachloride. To a solution of adamantane (1.2 g, 9 mmol) in 31 ml of CCl4 was added a finely pulverized mixture of silver bromide (1.7 g, 9 mmol) and silver acetate (1.5 g, 9 mmol). The mixture was stirred at reflux for 24 hr and then permitted to stand for an additional 5 days. At this point yields were determined on the supernatant liquid directly. Volatile by-products were determined by the use of quantitative external standards. Successive gas chromatographic injections reproduced peak areas with a precision of ±1%. Methyl chloride, phosgene (9%), and chloroform (33%, elution order) were determined at a column temperature of 23°; programming to 45° was necessary in order to determine the yield of bromotrichloromethane (8%). Acetic acid (78%, column B[20]) was determined at 70° and its identity as well as chloroform's was established by collection and comparison of the spectra with those of the authentic materials. The odor of phosgene was immediately apparent but its identity could be more rigorously established by the presence of its carbonyl absorption at 1828 cm^{-1} in the infrared spectrum of the supernatant. Following bromotrichloromethane analysis the column was programmed to 120°, whereby analysis of the adamantyl products was carried out over a programming range of 40° as a product ratio. The yield of unchanged adamantane as deduced from this ratio was in excellent agreement with the figure arrived at from a quantitative external standard evaluation. Identification of products was rigorously established, after isolation from the column, by comparison of the spectra with those of the authentic sample. Yields were as follows (elution order): adamantane (15%), 1-chloroadamantane (40%), 2-chloroadamantane (7%), 1,3-dichloroadamantane (15%), unidentified products (23%). Bromine was confirmed according to ref 12 and hydrogen chloride was determined by extracting the carbon tetrachloride solution with water (3 × 20 ml) and precipitating silver chloride by the addition of silver nitrate solution. This precipitate was pure white, turned purple on exposure to light, and was readily soluble in ice-cold 6 N NH4OH. As a control and to show that the precipitate did not arise from hydrogen bromide, silver bromide was precipitated from an authentic HBr solution. This precipitate was distinctly yellow, turned green on exposure to light, and was insoluble in 6 N NH4OH. The presence of hydrogen chloride also was obvious by the presence of a fuming acidic gas emanating from the reaction flask. An infrared spectrum of the silver salt mixture revealed that silver acetate was not present. If silver acetate and silver bromide are refluxed in carbon tetrachloride without adamantane, the mixture darkens considerably but silver acetate is not consumed.

3-Chloro-1-adamantyl Acetate (2). Method A. Reaction of 1-Bromoadamantane with Silver Acetate in Carbon Tetrachloride. A mixture of bromide 1 (1.0 g, 5 mmol), silver acetate (1.1 g, 7 mmol), and carbon tetrachloride (25 ml) was stirred at reflux for 24 hr. After an additional 4 days of standing the yields of adamantyl products were determined directly on the supernatant liquid as described in the preceding section (in order of elution): 1-chloroadamantane (4%), 1-adamantyl acetate (36%), 3-chloro-1-adamantyl acetate (2, 50%), unidentified products (10%). The yield of acetic acid was 82% and the other by-products such as CHCl3, BrCCl3, Br2, and HCl were qualitatively identified. Washing of the CCl4 solution with aqueous sodium carbonate, drying (MgSO4), and removal of solvent afforded 1.0 g of a light yellow liquid from which the adamantyl products were isolated by preparative gas chromatography. Chloroacetate 2 initially elutes as an oil which crystallizes upon standing. Its spectral properties have been described in the introductory section.

Anal. Calcd for C12H17ClO2: C, 62.90; H, 7.49; Cl, 15.46. Found: C, 62.91; H, 7.43; Cl, 15.55.

Method B. Reaction of 1-Adamantyl Acetate with Silver Bromide and Silver Acetate in Carbon Tetrachloride. A mix-

ture of 1-adamantyl acetate (**3**, 1.5 g, 8 mmol), silver acetate (1.3 g, 8 mmol), and silver bromide (1.5 g, 8 mmol) in 25 ml of carbon tetrachloride was stirred at reflux for 30 hr and then allowed to stand for an additional 10 days. At this point a 77% yield of acetic acid was determined from the supernatant liquid directly. Phosgene, methyl chloride, chloroform, and bromotrichloromethane were identified qualitatively. The adamantyl products were isolated by preparative gas chromatography in the following yields (elution order): 1-chloroadamantane (5%), 1-adamantyl acetate (22%), 3-chloro-1-adamantyl acetate (**2**, 62%), unidentified products (11%).

Reaction of Adamantane with Silver Bromide in Carbon Tetrachloride. Adamantane (1.0 g, 7 mmol) in 30 ml of carbon tetrachloride was stirred at reflux in the presence of 2.0 g (11 mmol) of silver bromide for 24 hr. After standing for an additional 3 days an 11% yield of 1-chloroadamantane was computed. At this point the gas chromatography peaks due to 2-chloroadamantane and 1,3-dichloroadamantane were too small to be reliably evaluated. It was, however, possible to identify bromine[12] and after an additional 7 days of standing it was possible to reliably compute the yields of all products reported as follows: phosgene (17%), bromotrichloromethane (13%). A quantitative external standard served to establish a 61% yield of unchanged adamantane while the ratio of adamantyl products was 1-chloroadamantane:2-chloroadamantane:1,3-dichloroadamantane, 76:10:19. Hydrogen chloride and bromine were also identified.

Chlorination of Adamantane with Bromine in Carbon Tetrachloride. To a solution of adamantane (1.2 g, 9 mmol) in 42 ml of carbon tetrachloride was added with stirring over a period of 27 hr a solution of bromine (0.8 g, 5 mmol) in 50 ml of carbon tetrachloride. After 6 days of stirring at room temperature the bromine color dissipated completely and at this point gas chromatographic analysis of the solution revealed the following yields: adamantane (6%), 1-chloroadamantane (40%), 1-bromoadamantane (2%), 1,3-dichloroadamantane (21%), unidentified products (31%).

Chlorination of Adamantane with Bromine Chloride. A 10% (w/v) solution of bromine chloride in carbon tetrachloride was prepared by adding bromine (11.80 g, 7.4 mmol) to a solution of chlorine (5.24 g, 7.4 mmol) in 90 ml of CCl₄.[21] With additional solvent the volume of solution was brought up to 170 ml. A uv spectrum of the solution displayed a single λ_{max} at 374 nm.

A 14-ml aliquot of the bromine chloride solution (12 mmol of BrCl) was diluted with additional CCl₄ to give a total volume of 40 ml and this was added with stirring over a period of 8 hr to a solution of adamantane (1.6 g, 12 mmol) in 30 ml of carbon tetrachloride. It took approximately 20 min for the last traces of halogen color to fully discharge. After an additional 20 hr of stirring the product yields were determined on the solution directly: bromotrichloromethane (30%), adamantane (19%), 1-chloroadamantane (25%), 2-chloroadamantane (5%), 1-bromoadamantane (5%), 1,3-dichloroadamantane (19%), unidentified products (27%). The solution was twice extracted with water and 1.0 g of silver chloride was precipitated by treating the washings with silver nitrate solution (60% yield of HCl). Hydrogen bromide could not be detected.

Chlorination of Adamantane with Bromine Chloride in the Presence of Silver Acetate. The procedure here was carried out in the exact manner as the one described above except that silver acetate (2.0 g, 12 mmol) was initially suspended in the adamantane solution before the addition of halogen was begun. After a 6-hr ad-

dition and 20 hr of stirring the following yields were determined from the supernatant liquid directly: adamantane (16%), 1-chloroadamantane (46%), 2-chloroadamantane (4%), 1-bromoadamantane (trace), 1,3-dichloroadamantane (16%), unidentified products (18%), bromotrichloromethane (18%), acetic acid (101%).

Registry No.—**2**, 53906-99-3; **3**, 19066-22-9.

References and Notes

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(20) Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer 257 grating spectrophotometer in CCl₄ or CS₂ in cavity cells. Uv spectra were recorded on a Perkin-Elmer 202 ultraviolet–visible recording spectrophotometer. A Varian A-60 spectrophotometer was used to record nmr spectra in CCl₄ using tetramethylsilane as an internal standard. Yields were determined by gas chromatography on a Hewlett-Packard 720 dual-column gas chromatograph. With the exception of acetic acids all products were determined on a 4 ft × 0.25 in. column of 20% SE-30 on Chromosorb W (column A). For acetic acid a 2 ft × 0.25 in. column of 20% DEGS on Chromosorb W, AW (column B) gave good results. Helium flow rates of 30–40 ml/min were found optimal. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.
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