












TABLE II
LiClO₄ REARRANGEMENT PRODUCTS

Reactant	Products
	 93%  5%
	 62%  4%  34%
	Olefins (see text) 5%  12%  36%  46%

D. LiClO₃-LiClO₄ Eutectic.—The eutectic consisted of 70 wt % LiClO₃ (7.0 g of LiClO₃ and 3.0 g of LiClO₄), mp 97°. ³

No special procedures were used to dry the salts except for the LiClO₃, which was heated to a temperature slightly above its melting point under vacuum.

Columns.—The salts were put onto the solid support by dissolving them in water or ethanol (100%) and removing the solvent with a rotary evaporator. This process also served to mix the salts of the eutectic. The melting point of the LiBr-RbBr salt on the support was determined using differential thermal analysis. A loading of 50% was used to increase sensitivity, and the melting point was 275–280°. This value is slightly higher than the

bulk melting point and may reflect some interaction with the solid support. The coated support was packed into 5 ft × 0.25 in. o.d., 0.020 in. wall stainless steel tubing by gravity and the column was purged with helium at ~10° above the desired operating temperature for several hours.

Epoxides.—The epoxides were obtained from Dr. Rickborn, prepared from the corresponding olefins by the method of Korach¹¹ or purchased commercially. All were greater than 95% pure as determined by gc.

Rearrangements.—The epoxide as injected in 50-μl. portions onto the column until enough material was collected (~0.5 ml) for analysis. The carrier gas was helium. The products were trapped in small bulbs immersed in either a solid CO₂-acetone or ice-salt bath. The gc columns used for analysis and collection were 10 ft × 0.25 in. 10% Carbowax 20 M on 60–80 mesh Chromosorb W, 10 ft × 0.25 in. 10% Carbowax 4000 on 60–80 mesh Chromosorb W, and 15 ft × 0.25 in. 10% silicone gum rubber on 60–80 mesh Chromosorb W.

Registry No.—LiBr, 7550-35-8; LiClO₄, 7791-03-9; RbBr, 7789-39-1.

Acknowledgment.—The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work. One of the authors (C. B.) also wishes to acknowledge financial support from the National Science Foundation Undergraduate Research Program. The authors also thank Dr. B. Rickborn for helpful advice and several samples of compounds used in this study.

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Chlorination of Adamantane by Ferric Chloride and Antimony Pentachloride¹

PETER KOVACIC* AND JU-HUA CHEN CHANG²

Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

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In various solvent systems, the reaction of ferric chloride or antimony pentachloride with adamantane yielded mainly chloroadamantane along with some 1,3-dichloroadamantane. High yields of hydrogen chloride and the reduced form of the salt were also obtained. With longer reaction times the chloroadamantane isomers underwent extensive interconversion. In isomerization studies carried out with the individual isomers and the metal halides, some disproportionation and chlorination occurred. Initial 1:2 isomer ratios (~6) were estimated by performing the chlorinations for short periods at higher temperatures. These values are close to the 1:2 ratios reported in the literature for radical processes involving adamantane but different from the figures for ionic ones. In the case of ferric chloride, no catalytic effect was exerted by aluminum chloride, water, or light. Photolysis enhanced the rate of the antimony pentachloride process. The ferric chloride reaction is probably a nonchain process, whereas antimony pentachloride may be involved in a radical chain sequence. A high 1:2 ratio was observed with SbCl₅-AlCl₃, indicating a polar pathway.

Relatively little attention has been devoted to the reactions of ferric chloride and antimony pentachloride with C-H linkages in organic compounds. About 10 years ago, it was reported that ferric chloride reacts with alkanes under mild conditions, with the order of reactivity being tertiary > secondary.³ Although no pure entities were isolated from the complex organic product, the reaction was characterized by evolution of hydrogen chloride and reduction of Fe(III) to Fe(II). Methylcyclohexane, which was examined in greater detail,⁴ yielded solid polymer along with a small amount

of (methylcyclohexyl)toluene. In a related area, investigations of ferric chloride and alkylbenzenes disclosed the occurrence of various competing reactions including di- and triarylmethane formation from side-chain attack.^{5–8} Ultraviolet irradiation of toluene and ferric chloride-lithium chloride in acetic acid gave benzyl chloride and ferrous chloride.⁹ In relation to functionalities other than hydrocarbons, ferric chloride

(1) Paper II: Adamantanes and Related Compounds; preliminary communication, *Chem. Commun.*, 1480 (1970); for the previous paper in the series, see P. Kovacic and P. D. Roskos, *J. Amer. Chem. Soc.*, **91**, 6457 (1969).

(2) From the M. S. Thesis of J.-H. C. C., 1970.

(3) P. Kovacic and H. C. Volz, *J. Amer. Chem. Soc.*, **81**, 3261 (1959).

(4) P. Kovacic, S. T. Morneweck, and H. C. Volz, *J. Org. Chem.*, **28**, 2551 (1963).

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(6) P. Kovacic and C. Wu, *J. Org. Chem.*, **26**, 759, 762 (1961).

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effected mono- or dichlorination at the α position of cyclic ketones in acetic acid.¹⁰ Secondary and tertiary aliphatic amines formed violet products, presumably from attack on hydrogens α to the nitrogen, accompanied by reduction of the metal halide.¹¹

Several investigators have studied the interaction of antimony pentachloride with alkanes. Krause noted¹² the presence of methyl chloride among the products formed from methane at 300°. Later, the reaction with alkanes was examined as an analytical method for determining tertiary hydrogen content.^{13,14} In cursory explorations, Volz observed¹⁵ that methylcyclohexane reacted readily at low temperatures; no pure organic product was isolated. ESR spectral studies were reported¹⁶ for radicals generated from the metal halide and various alkanes. Antimony pentachloride is known to bring about side-chain attack with certain alkylbenzenes, forming diarylmethanes and polymer,¹⁷ or hexachloroantimonate salts of stable carbonium ions.¹⁸ Alkyl chlorides afforded the next higher chloro homolog, as in the formation of ethylene dichloride from ethyl chloride.¹⁹ Substitution of a primary hydrogen was less favorable than either secondary or tertiary.

The aim of the present work was to aid in elucidating the mechanistic aspects of the alkane reaction with ferric chloride and antimony pentachloride. Because of its favorable features, adamantane was selected as the substrate.

Results and Discussion

Ferric Chloride.—Adamantane and ferric chloride (1:2.2 molar ratio) in carbon tetrachloride at reflux for 54 hr gave 64–72% yields of chloroadamantane possessing a 1:2 isomer ratio of 12–15. The effects of variation in solvent, temperature, and time were investigated (Table I). In stannic chloride, 1,1,2-trichloro-1,2,2-trifluoroethane, methylene chloride, or methylene chloride–carbon tetrachloride at 40–48° for times less than 24 hr, the amount of chloroadamantane was quite low (1:2 ratios of 20–42, usually). At 110° in stannic chloride for 7 hr, the yield of principal product increased to about 60% (1:2 ratio of about 13). Photolytic conditions did not promote the reaction. No chlorination was observed in stannic chloride in the absence of ferric chloride.

When the yield of monochloro derivative was greater than 56%, 1,3-dichloroadamantane was also present to the extent of 6–28%. In a more thorough analysis of the carbon tetrachloride system, it was found that hydrogen chloride (109–130%) and ferrous chloride (106–108%) were also generated.

Work-up of the reaction mixtures entailed exposure to concentrated hydrochloric acid. When basic conditions were used, appreciable amounts of 1-adamantanol

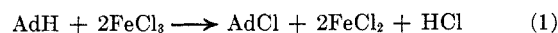
TABLE I
CHLORINATION OF ADAMANTANE BY FERRIC CHLORIDE^a

Solvent (ϵ)	Temp, °C	Time, hr	—Chloroadamantane—		Dichloro-
			Yield, %	1:2 ratio	adamantane yield, ^b %
CCl ₄ (2.24)	78	6.5 ^c	4	11	..
		54	64–72	12–15	6–16
CH ₂ Cl ₂ (9.08)	40°	7	2	20	..
		10	4	28	..
CH ₂ Cl ₂ –CCl ₄	48	2.5 ^c	3	42	..
		4.5	3–6	27–42	..
		7	8–9	23–30	..
SnCl ₄ (2.87)	40°	24	<1	7	..
SnCl ₄ (2.87)	110	3	23–58	9–10	.., 22
		7	56–60	12–14	20–28
CCl ₂ FCClF ₂ (2.41)	40°	24	1
CCl ₂ FCClF ₂ (2.41) ^d	40°	24	0.3

^a Molar ratio, adamantane:FeCl₃ = 1:2.2. ^b Blank indicates negligible yield. ^c Single run. ^d Plus AlCl₃ (4.4 g, 0.033 mol).

and adamantanone were present, apparently from hydrolysis and oxidation. The reactions were carried out under nitrogen.

Apparently, chlorination proceeds in a redox manner as depicted. Since it is reasonable to expect isomeriza-



tion of chloroadamantanes in the presence of a Friedel-Crafts catalyst, several studies of this aspect were carried out. Exposure of 1-chloroadamantane to excess ferric chloride in carbon tetrachloride at reflux for 2–5 hr afforded chloroadamantanes (1:2 = 15–21) with about 70% recovery (Table II). In titanium tetrachloride at 134° for 5–15 min the ratio was 10 (about 40–60% recovery) (Table III). Adamantane and dichloroadamantane were also present in both cases. The close correspondence between these data and the ratios for the adamantane reactions indicate that equilibration has been closely approached under the conditions of chlorination. Of course, the observed ratios must be taken as approximate indications of the true equilibrium values because of disproportionation and chlorination of chloroadamantane.

On consideration of the recent finding²⁰ from Schleyer's laboratory concerning the mechanism of rearrangement of 2-adamantanol to 1-adamantanol under acidic conditions, isomerization of chloroadamantanes may well proceed intermolecularly *via* carbonium ion intermediates, rather than by a simple 1,2-hydride shift. Disproportionation quite likely involves intermolecular hydride abstraction.

In line with our principal aim of elucidating the nature of the initial step, we examined² the halogenation reaction at short reaction times in order to minimize rearrangement. In titanium tetrachloride at 134°, ferric chloride and adamantane produced chloroadamantanes which displayed 1:2 ratios increasing from 7 to 9 during the 10–20-min time interval. A figure of about 6 resulted from extrapolation to zero time. In a repeat run, the extrapolated value was 8 from a 1–3-min time interval. Titanium tetrachloride alone

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(19) V. Meyer and F. Müller, *J. Prakt. Chem.*, **46**, 161 (1892).

TABLE II
 ISOMERIZATION OF CHLOROADAMANTANE BY METAL HALIDES AT LOWER TEMPERATURES

Substrate	Metal halide	Time, hr	Yield, %			Dichloroadamantane	1:2 AdCl ratio
			X = H	X = 1-Cl	X = 2-Cl		
1-ClAd	SbCl ₅ ^a	2-3	10-12	66-71	3-4	17-18	15-21
	FeCl ₃ ^a	2-5	9-12	67-70	3-5	17-18	15-21
	AlCl ₃ ^{b,c}	0.25-1	9-11	74-76	2	12-15	33-36
2-ClAd	SbCl ₅ ^a	3-4.5	9-11	56-67	9-15	8 ^d -18 ^d	5-8
	AlCl ₃ ^b	1-3	10-12	75-75	2-3	11-12	30-39

^a In CCl₄, 78°. ^b In CCl₂FCClF₂, room temperature. ^c A control reaction of adamantane-AlCl₃-CCl₂FCClF₂ at room temperature, 1 hr, gave no chlorination product. ^d Additional 10% of two unidentified components (dichloroadamantanes?).

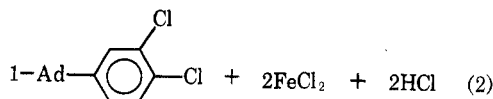
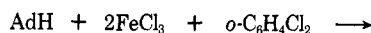
 TABLE III
 ISOMERIZATION OF 1-CHLOROADAMANTANE BY METAL HALIDES AT HIGHER TEMPERATURES

Metal halide	Time, min	Yield, %			Dichloroadamantane	1:2 AdCl ratio
		X = H	X = 1-Cl	X = 2-Cl		
SbCl ₅ ^a	30-60	8-9	64-65	4-5	22-23	13-16
FeCl ₃ ^b	5-15	2-6	42-61	4-6	21-43	10-10

^a In SnCl₄, 110°. ^b In TiCl₄, 134°.

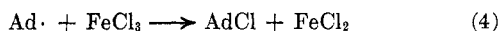
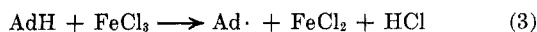
did not function as a halogenating agent under these conditions.

A different product was isolated when the reaction was conducted in *o*-dichlorobenzene at 103°. The nmr and infrared spectra, in addition to microanalyses, pointed to 1-(1,2-dichloro-4-phenyl)adamantane. Equation 2 may be written for the reaction, which also

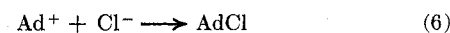


generates hydrogen chloride. Presumably the adamantyl cation is involved (*vide infra*, eq 4 and 5). We did not ascertain whether or not there was any 2-adamantyl isomer present in the crude material. The properties (melting point, ir, and glpc behavior) appeared identical with those of authentic material which was obtained by Friedel-Crafts alkylation²¹ of *o*-dichlorobenzene with 1-bromoadamantane. Attempted high-temperature oxidation with dichromate²² to 3,4-dichlorobenzoic acid did not meet with success. As far as we are aware, this represents the first example of aromatic alkylation by adamantane. Generally, derivatives of the parent, *e.g.*, bromoadamantane^{21,23,24} and 1-adamantyl chloroformate,²⁵ have been used.

We favor a radical mechanism for rationalization of the experimental results.



Alternatively, the adamantyl radical might participate as indicated below.



According to these schemes, a chain process does not

(21) H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, **92**, 1629 (1959).

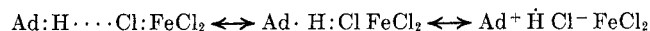
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(24) H. Stetter and M. Krause, *Tetrahedron Lett.*, 1841 (1967).

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pertain. Ease of reduction²⁶ and the paramagnetism^{27a} of ferric chloride can be considered driving forces for eq 3, 4, and 5. In relation to eq 3, a similar molecule-induced homolysis has been proposed for the alkane-oxygen combination.^{28a} Even certain pairs of nonradical species, *e.g.*, methane and fluorine, are believed to combine *via* a homolytic process.^{28b} There is experimental analogy for eq 4, since ferric chloride is known to be a scavenger of carbon radicals.^{29,30} The form in which the metal halide participates is not known, $(\text{FeCl}_3)_n \rightleftharpoons (\text{FeCl}_3)_2 \rightleftharpoons \text{FeCl}_3$. It is reported³¹ to exist as the dimer in nonpolar solvents and as a solvated monomer in more polar media, such as ether. Because of the good thermal stability of ferric chloride at our operating temperatures, involvement of chlorine from thermal dissociation should be negligible.^{27b} The slight favorable effect on rate from use of a solvent of relatively high dielectric constant (Table I) may result from conversion of the salt to a more active form. Alternatively, the solvent effect may reflect the contribution of polar forms to the resonance hybrid in the transition state.



A similar situation has been described for hydrogen abstraction reactions involving chlorine atoms.^{28c}

The general hypothesis is in keeping with various lines of evidence from our own work, as well as from the findings of others. A principal argument rests in a comparison with radical halogenation of adamantane. The literature³²⁻³⁵ records values of 0.6-2.1 (1:2 ratio) for

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halogenation of adamantane with chlorine or sulfonyl chloride under photolytic conditions. Our own data (0.5–0.6) (Table IV), obtained with chlorine in meth-

TABLE IV
CHLORINATION OF ADAMANTANE WITH CHLORINE

Solvent	Temp, °C	Time, min	—Chloroadamantane ^a —	
			Yield, %	1:2
CH ₂ Cl ₂ ^b	40	180	18	0.5
SnCl ₄ ^b	98–100	5	8	0.6

^a Glpc showed the presence of less volatile products also.
^b Single run.

ylene chloride (40°) or stannic chloride (100°), correspond closely to the earlier report; initiation might be molecule induced, by room light, or by adventitious initiator in the system. Furthermore, photolytic bromination³⁴ gave a figure (1.8) in the same range. The slightly higher ratios with ferric chloride can be attributed to increased selectivity of the abstracting entity, which has ample precedence in the literature.³³ Other radical species also give low 1:2 ratios, <7, on interaction with adamantane.^{33,34,36}

Various lines of evidence, both from these and earlier studies, argue against a polar pathway. No catalysis (Tables I and V) was observed at 40 or 103° on addition

TABLE V
ALKYLATION OF *o*-DICHLOROBENZENE BY
ADAMANTANE IN THE PRESENCE OF FERRIC CHLORIDE^a

Reactions ^b	Initiation temp, °C	Time, ^c hr	HCl, %
AdH-FeCl ₃ -ODCB	103	3	88
AdH-FeCl ₃ -ODCB-AlCl ₃ ^d	99–100	4	102
AdH-FeCl ₃ -ODCB-H ₂ O ^e	100	3.3	78
AdH-FeCl ₃ -ODCB ^f	102–103	3	70
AdH-FeCl ₃ ·6H ₂ O-ODCB	103 ^g	1	

^a Molar ratio, AdH:FeCl₃ = 1:2.3. ^b Single run. ^c Total time after initiation; time to reach initiation temperature was 50–90 min. ^d AdH:FeCl₃:AlCl₃ = 1:2.3:1.05. ^e AdH:FeCl₃:H₂O = 1:2.3:0.6. ^f Anhydrous conditions. ^g Heated at 103° for 1 hr; no hydrogen chloride was detected.

of aluminum chloride, based on initiation temperature and reaction rate² (*cf.* SbCl₅ section). Furthermore, there was no indication of cocatalysis by water either from the initiation temperature (Table V) or rate of reaction.²

It is quite revealing that halogenation of this substrate with SbCl₅-AlCl₃ gave 1:2 ratios >90 (see SbCl₅ section). There is general agreement that designation in the polar category applies to a number of halogenation procedures³⁷ with adamantane, namely, chlorination with *tert*-butyl chloride-aluminum chloride and bromination with bromine. We modified the *tert*-butyl chloride technique by using stannic chloride as catalyst at 111° in order to minimize product rearrangement. The chloroadamantanes displayed a 1:2 ratio ≥1000:1. With aluminum chloride at room temperature, the figures generally fell in the 20–50 range, evidently reflecting the occurrence of rearrangement. There is no mention of the 2 isomer in the previous work.³⁸ We

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(38) K. Gerzon, E. V. Krumkalns, R. L. Brindle, F. J. Marshall, and M. A. Root, *J. Med. Chem.*, **6**, 760 (1963).

observed that exposure of 1- or 2-chloroadamantane to aluminum chloride at room temperature for 0.25–3 hr gave 1:2 ratios of 30–39 (about 77% recovery, along with disproportionation products). Aluminum chloride alone does not function as a chlorinating agent. Also, chlorination with ferric chloride in carbon tetrachloride differs mechanistically from the AlCl₃-CCl₄ system,³⁹ since ferrous chloride is generated in the former case. All of the investigators on bromination report only the bridgehead isomer, as evidenced by glpc³³ and nmr²¹ data. Nitration also proceeded by highly selective attack at the tertiary position.³³ In general, ionic reactions of adamantane afford higher 1:2 ratios than do radical types.³⁷

Small quantities of chloroform were detected in a number of the ferric chloride (and antimony pentachloride) reactions carried out in carbon tetrachloride. Since the same component was observed with aluminum chloride, the mechanistic significance is unclear.

Olah and coworkers^{40,41} have recently announced an interesting new reaction of onium species with the C-H bonds of adamantane and other alkanes, which is believed to entail pentacoordinate carbon. For example, a ratio of 19 resulted from nitration with nitronium tetrafluoroborate. Similar transformations apparently occur with protons and certain carbonium ions—the very potent Lewis acids.

It is pertinent to review briefly the known chemical behavior of the Cl-Fe bond in ferric chloride in relation to our postulated mechanism. As mentioned earlier (*vide supra*), the linkage readily undergoes homolytic fission.^{29,30} Also, polarization of the type Fe³⁺Cl₃¹⁻ is well established.³¹ On the other hand, we know of no definitive case in which the chlorine assumes positive character. A number of studies have been reported on aromatic chlorination by ferric chloride. The indicated possibilities have been advanced^{7,8,42–44} for the reaction pathway about which there is still considerable uncertainty: attack by Cl^{δ+}, intermediate radicals, organometallic species, or charge-transfer complexes. Considering all of the data from the various sources, we believe it reasonable to classify the adamantane-ferric chloride reaction in the radical category.

There are pronounced differences in the nature of the end products between the present report and earlier investigations with simpler alkanes. In the prior work^{3,4} the reaction mixtures from substrates, such as methylcyclohexane, were considerably more complicated. Evidently, the rather clean process with adamantane reflects resistance of the halide to dehydrohalogenation even in the presence of Friedel-Crafts catalysts. With alkanes devoid of this stabilizing feature, alkenes can be generated and then subsequently undergo a variety of reactions.¹⁴ It is reasonable to apply the same mechanistic hypothesis to other substrates, *e.g.*, alkanes and aralkyls, undergoing interaction between ferric chloride and C-H linkages.^{3,4,7,8} In prior investigations^{3,4,8} both radical and polar pathways had

(39) H. Stetter, M. Krause, and W.-D. Last, *Angew. Chem., Int. Ed. Engl.*, **7**, 894 (1968).

(40) G. A. Olah, unpublished data.

(41) G. A. Olah and G. D. Mateescu, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970.

(42) P. Kovacic and R. M. Lange, *J. Org. Chem.*, **30**, 4251 (1965).

(43) P. Kovacic and F. W. Koch, *ibid.*, **28**, 1864 (1963).

(44) D. Z. Denney, T. M. Valega, and D. B. Denney, *J. Amer. Chem. Soc.*, **86**, 46 (1964).

been advanced as possibilities. Since firm evidence was lacking, the interpretations would be classified as highly speculative.

Antimony Pentachloride.—Adamantane and antimony pentachloride in carbon tetrachloride at reflux for 36 hr gave chloroadamantane, 66–79% yield, 1:2 molar ratio of 11–16. Reactions were performed under nitrogen. As shown in Table VI, a number of variables

TABLE VI

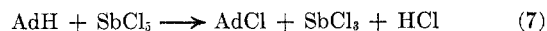
CHLORINATION OF ADAMANTANE BY ANTIMONY PENTACHLORIDE^a

Solvent ^b	Temp, °C	Time, hr	Chloroadamantane		Dichloro-
			Yield, %	1:2 ratio	adamantane yield, %
CCl ₄	78	3	7–9	11–15	
		4	14–20	13–15	
		36	66–79	11–16	4–13
CH ₂ Cl ₂	40	0.5 ^d	24	31	
		1	40–42	35–39	
		3	68–70	36–42	
CH ₂ Cl ₂ –CCl ₄	48 ^d	2	52	22	
		5	75	21	6
		6.5	76	22	8
SnCl ₄	40	1	10–13	17–18	
		3	13–19	19–21	
		5 ^d	20	16	
SnCl ₄	110	0.25	23–33	9–10	
		1	59–56	10–11	4–8
		3	74–70	12–13	4–9
SnCl ₄ ^e CCl ₂ FCClF ₂	110 ^d 40	1			
		2 ^d	5	21	
		3	7–8	18–21	

^a Molar ratio, adamantane:SbCl₅ = 1:1.1. ^b ϵ for SbCl₅ is 3.22. ^c Blank indicates negligible yield. ^d Single run. ^e In the absence of SbCl₅.

were explored. Good yields were obtained in stannic chloride at 110° and in methylene chloride at 40°. The reaction at 40° was appreciably faster in methylene chloride (relatively high dielectric constant) than in stannic chloride or 1,1,2-trichloro-1,2,2-trifluoroethane. The 1:2 ratios generally fell in the 10–20 range, except with methylene chloride as the medium (30–40).

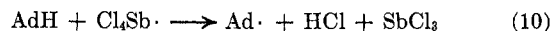
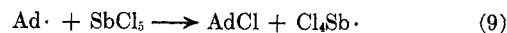
When chloroadamantane was generated in quantities greater than 56%, 1,3-dichloroadamantane appeared as a by-product (4–13%). A scrutiny of the reaction in carbon tetrachloride revealed the formation of hydrogen chloride (123–138%) and antimony trichloride (108%). Chlorination appears to proceed as illustrated.



From isomerization studies (Table II), exposure of 1-chloroadamantane to an equimolar amount of the metal halide at reflux for 2–3 hr gave chloroadamantane with 1:2 of 15–21 (65–70% recovery). Adamantane and dichloroadamantane were formed as a result of disproportionation; the unequal quantities presumably reflect an alternate route (chlorination) for arriving at the dichloro stage. With the 2-chloro isomer, the 1:2 ratio was 5–8, with somewhat less recovery. Dichloroadamantane formation appeared to be a more serious competing reaction in this case. The close correspondence between these values and the ratios from the adamantane reaction in carbon tetrachloride indicates that equilibrium has been attained or closely approached at the end of chlorination.

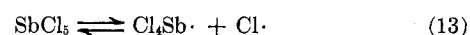
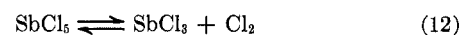
Attempts to obtain initial 1:2 ratios from short reaction times proved successful under the appropriate conditions.² In stannic chloride at 110°, the figure increased from 5 to 7 during 1 to 5 min with an extrapolated ratio of 4.

Our mechanistic preference is for a radical pathway involving oxidation–reduction (eq 8–11). The rami-



fications are broader than in the case of ferric chloride. The steps set forth in eq 8–10 comprise a chain process. In addition, processes analogous to eq 5 and 6 may be operative.

Although antimony pentachloride (less stable than ferric chloride) exhibits little decomposition^{27c,45} below 120°, we cannot be sure of the exact extent to which preliminary dissociation (eq 12 and 13) contributes to



chlorination. It is reasonable to expect greater participation at higher temperatures and extended reaction times. The free-radical concept is in line with rate enhancement from photolysis (Table VII). However,

TABLE VII

PHOTOLYTIC CHLORINATION OF ADAMANTANE BY ANTIMONY PENTACHLORIDE

Time, min	Chloroadamantane yield, %		Control
	Lamp distance, ^a in.		
	3	15	
5	59	31	4–6
10	61	35	5–11
15	74	58	23–33
60	75 ^b	68	63–64

^a Single runs; 1:2 ratios of 8–11; plus 1,3-dichloroadamantane (<12%). ^b In the absence of metal halide, chlorination did not take place.

it is not clear whether the light catalyzes eq 8–11 or eq 12 and 13.

As in the case of ferric chloride, it is significant that the 1:2 ratios are in close agreement with those observed with known radical processes, and are lower, considerably so in most cases, than the figures for substitutions which are unequivocally polar. A highly important result was made available from use of the antimony pentachloride–aluminum chloride combination at 40°. For short reaction periods (20–30 min) 1:2 ratios >90 were observed for chloroadamantane (Table VIII).

TABLE VIII

CHLORINATION OF ADAMANTANE WITH ANTIMONY PENTACHLORIDE–ALUMINUM CHLORIDE

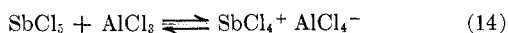
Time, min	Chloroadamantane	
	Yield, %	1:2 ratio
20	2–3	>90
30	4–6	>90
120	24–25	28, 39
180	31–39 ^a	36, 300

^a 2–3% Dichloroadamantane.

(45) H. Braune and W. Tiedje, *Z. Anorg. Allg. Chem.*, **152**, 39 (1926).

When the time was extended (2–3 hr), the values decreased to 25–40 in general, presumably from rearrangement. In one case, the figure was 300, indicating incomplete equilibration. It would appear that the catalytic potency of aluminum chloride is decreased in this system, possibly due to coordination with antimony chlorides. These represent the highest 1:2 ratios obtained from an inorganic chlorinating agent, approaching those from uncatalyzed bromination and *tert*-butyl chloride–stannic chloride. The presence of aluminum chloride also increased the rate of chlorination (*cf.* Table VI), which comprises additional evidence for a polar mechanism.

As background for interpretation, one should consider the state of antimony pentachloride when in contact with Friedel–Crafts catalysts. For the metal halide itself in the appropriate solvent^{46,47} the evidence points to dimer formation resulting in the indicated ionization, $\text{SbCl}_4^+ + \text{SbCl}_6^-$. Furthermore, there are reports of the existence of SbCl_4^+ (presumably as part of an ion pair) in the systems $\text{SbCl}_4\text{F} - \text{AsF}_3$ ⁴⁸ and $\text{SbCl}_5 - \text{SbCl}_3$.⁴⁹ By analogy, it is reasonable to expect the indicated coordination in our case. In relation to the



more detailed aspects of the polar route, attack on the C–H bond could conceivably involve hydride abstraction¹⁵ or pentacoordinate carbon.⁴¹ Also, the interacting moiety in SbCl_4^+ might be either Sb or Cl, most likely the latter.

Holmes and Pettit commented¹⁸ briefly on possible mechanistic pathways for conversion of hydrocarbons, such as cycloheptatriene and triphenylmethane, to carbonium ion salts by means of antimony pentachloride. Direct hydride abstraction appeared to be the simplest explanation. A charge-transfer reaction was considered as an alternative. Other investigators have also invoked the concept of charge-transfer in reactions of antimony pentachloride. Quite plausible examples were reported by Aalbersberg and coworkers,⁵⁰ who observed carbonium ion formation from interaction with polynuclear hydrocarbons, *e.g.*, anthracene and perylene. Also, mechanistic application was made to the reaction with 1,1-diphenylethylene.⁴⁷ Although charge transfer cannot be ruled out conclusively in the present work, we deem it a less likely possibility.

Fukui and coworkers¹⁶ provided a detailed analysis of the esr spectra for radicals derived from alkanes and antimony pentachloride, but the intimate aspects of the initial interaction were not treated. They noted the evolution of hydrogen chloride and the order of reactivity, tertiary > secondary and primary. Radical cations of unsaturated hydrocarbons are thought to be generated. These alkanes possess an inherent disadvantage in that olefin formation quite likely occurs as a complicating feature.¹⁴

On the basis of our results, serious consideration should be given to the free-radical concept as an inter-

pretation of the prior reactions described for hydrocarbon C–H bonds and antimony pentachloride.

Antimony pentachloride reacts at a more rapid rate than ferric chloride. Various explanations can be offered: chain *vs.* nonchain reaction, and homogeneous *vs.* heterogeneous system. We do not know the redox potentials for the two salts in the solvent used.

Finally, the literature records various modes for the synthesis of 1-chloroadamantane. High yields are reported from the indicated precursors: 1-adamantanol,^{21,35,51} adamantane-1-carboxylic acid,⁵² 1-acetamidoadamantane,^{21,53} *N*-(1-adamantyl)methylurethane,^{53,54} *N*-(*p*-toluenesulfonyl)-1-aminoadamantane,^{53,54} 1-adamantyl chloroformate,²⁵ adamantane-*tert*-butyl chloride–aluminum chloride³⁸ (*cf.* isomeric purity from the present work), and adamantane–acetyl chloride–aluminum chloride.⁵⁵

Experimental Section

Materials.—High-purity commercial materials were used.

Analytical Procedures.—Infrared spectra were obtained on a Beckman IR-8 spectrophotometer with dilute solutions in carbon disulfide or carbon tetrachloride. Varian T-60 or HA-100 instruments were used to obtain nmr data. Gas chromatography was carried out with Varian Aerograph instruments (1700 or 1800) (thermal conductivity). The indicated columns were employed: (A) 15 ft × 0.25 in., 3% Carbowax 20M and 3% silicone DC 550 on acid-washed Chromosorb P (30–60 mesh), 160° column temperature, 94.6 ml/min.; (B) 5 ft × 0.25 in., 3% silicone SE-30 on Var-A-Port 30 (100–120 mesh), 200°; (C) 10 ft × 0.25 in., 20% SE-52 on acid-washed Chromosorb W (45–60 mesh), 100°, 64.5 ml/min for chloroform, 180°, 57.2 ml/min for 2-chloroadamantane peak enhancement; (D) 6 ft × 0.25 in., 20% TCP on acid-washed Chromosorb P (30–60 mesh), 100°, 64.5 ml/min.

Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Quantitative analyses for ferrous chloride and antimony trichloride⁵⁶ were performed as indicated. Potassium permanganate solution, prepared as described previously,⁵⁷ was standardized with arsenic trioxide. The aqueous portion from work-up of the reaction mixture was diluted to 250 ml with the acidic solution described in work-up procedure A. A 25-ml aliquot was titrated to a pink color. A control sample was prepared by mixing the metal halide and carbon tetrachloride, then following the general work-up procedure. Subtraction of the blank titration gave the corrected result.

The yield of hydrogen chloride was determined by titration with 1 *N* sodium hydroxide (phenolphthalein indicator) which was standardized with potassium hydrogen phthalate.

Chlorination of Adamantane. 1. General Procedure.—In general, duplicate runs were made. A 100-ml, three-necked flask was equipped with a mechanical stirrer, thermometer, nitrogen inlet, Friedrichs condenser, and hydrogen chloride trap, containing 25 ml of 1 *N* sodium hydroxide, protected by an Ascarite tube. With stannic chloride as solvent, a Dry Ice trap was included in order to minimize escape of solvent into the acid trap. The apparatus was flushed with nitrogen and then a moderate flow was maintained. Then 4.1 g (0.03 mol) of adamantane in 40 ml of carbon tetrachloride was added. At the reflux temperature was added either a solution of 9.87 g (0.033 mol) of antimony pentachloride in 20 ml of carbon tetrachloride

(51) P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 2700 (1961).

(52) L. F. Fieser, M. Z. Nazer, A. Archer, D. A. Berberian, and R. G. Slighter, *J. Med. Chem.*, **10**, 517 (1967).

(53) H. Stetter, M. Schwarz, and A. Hirschhorn, *Angew. Chem.*, **71**, 429 (1959).

(54) H. Stetter, J. Mayer, M. Schwarz, and C. Wulff, *Chem. Ber.*, **93**, 226 (1960).

(55) I. Tabushi, J. Hamuro, and R. Oda, *Nippon Kagaku Zasshi*, **98**, 794 (1968); *Chem. Abstr.*, **70**, 11198 (1969).

(56) P. Kovacic and A. K. Sparks, unpublished work.

(57) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Macmillan, New York, N. Y., 1952, pp 564–566.

(46) L. Kolditz and H. Z. Preiss, *Z. Anorg. Allg. Chem.*, **310**, 242 (1961).

(47) B. E. Fleischfresser, W. J. Cheng, J. M. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 2172 (1968).

(48) L. Kolditz, *Z. Anorg. Allg. Chem.*, **289**, 128 (1957).

(49) M. I. Usanovich, T. N. Sumarokova, and M. B. Beketov, *Izv. Akad. Nauk. Kaz. SSR, Ser. Khim.*, **3** (1953); *Chem. Abstr.*, **48**, 5703 (1954).

(50) W. I. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, 3055 (1959).

or 10.7 g (0.066 mol) of ferric chloride washed in with 20 ml of carbon tetrachloride. The mixture was kept at reflux for the desired length of time. After prolonged periods the yellow solution from antimony pentachloride, essentially homogeneous, turned dark in color, and the black ferric chloride mixture (heterogeneous) became dark brown.

Work-up was by one of two routes. In A, the reaction mixture was cooled with an ice bath, washed out with ether, and mixed with 1 *N* hydrochloric acid (200 ml) in the case of ferric chloride or 1 *N* hydrochloric acid-3 *N* sulfuric acid in the case of antimony pentachloride. The aqueous layer was separated and extracted once with ether; the combined organic portion was then washed twice with the same type of acidic solution as used in the work-up. After drying and evaporation of solvent, the residual material was dissolved in carbon disulfide for analysis. Yields were determined with glpc column A. This procedure was followed when the reaction mixture was analyzed for the reduced form of the metal halide.

In B, the reaction mixture was cooled somewhat and quenched with cold, concentrated hydrochloric acid. When an inorganic solvent was involved, carbon tetrachloride was introduced to dissolve the organic product. The layers were separated, and the nonaqueous portion was extracted twice with distilled water, dried over sodium sulfate, and freed of solvent.

After 36 hr, antimony pentachloride afforded chloroadamantanes, 66-79% (1:2 molar = 11-16), 1,3-dichloroadamantane, 4-13%, hydrogen chloride, 123-128%, and antimony trichloride, 108%. After 54 hr, ferric chloride gave chloroadamantanes, 64-72% (1:2 molar = 12-15), 1,3-dichloroadamantane, 6-16%, and ferrous chloride, 106-108%. For 1-3-hr reaction times with ferric chloride, erratic yields were obtained in stannic chloride. Yields are based on adamantane according to the stoichiometry in eq 1 and 7. In general, an internal standard was not used for yield determination; several checks with an internal standard showed the method to be valid. No statistical corrections were made in calculations of molar ratios for the chloroadamantane isomers.

Organic products were characterized by comparison with authentic materials (infrared spectra) and by physical constants: 1-chloroadamantane, mp 162.5-164°; 2-chloroadamantane, glpc peak enhancement with columns A and C; 1,3-dichloroadamantane, mp 131-132°; chloroform, glpc peak enhancement with columns C and D.

2. Short Reaction Times.²—A mixture of antimony pentachloride (9.87 g, 0.033 mol) and stannic chloride (20 ml) was preheated to 110° before addition to a mixture of adamantane (4.1 g, 0.03 mol) and stannic chloride (40 ml) at the same temperature. Following work-up procedure B, chloroadamantane was isolated and analyzed for the 1:2 isomer ratio. In the other case, ferric chloride (10.7 g, 0.066 mol) and titanium tetrachloride (20 ml) were heated separately to 134° before admixture.

3. Reaction Variables. A. Solvent Studies.—Stannic chloride, methylene chloride, and carbon tetrachloride-methylene chloride (equal volumes) were tested as solvents at several reaction temperatures (Tables I and VI). There was no detectable chloroform from the mixed solvent reaction.

B. Temperature Studies.—Various temperatures were used in order to ascertain the influence on yield and product distribution (Tables I and VI).

C. Photolytic Conditions.—A mixture of adamantane (4.1 g, 0.03 mol) and antimony pentachloride (9.87 g, 0.033 mol) in 60 ml of stannic chloride at 110° was exposed to a sunlamp, 660 W, 250 V, at distances of 3 or 15 in. (Table VII). With ferric chloride at 3 in. for 0.5 hr, the yield was 3%, in comparison with <1-4% for the control.

D. Effect of Water.—When ferric chloride hexahydrate (20.8 g, 0.077 mol) was used in place of the anhydrous material at 103° for 1 hr, neither hydrogen chloride nor organic product (glpc, column B) was formed (*o*-dichlorobenzene solvent).

E. Catalyst Study.—The data from addition of aluminum chloride (2.2 g, 0.0165 mol) to the standard system, adamantane-SbCl₅-CCl₂FCClF₂ (40°), are shown in Table VIII.

F. Basic Hydrolysis.—When work-up procedure B was modified by use of 4 *N* sodium hydroxide in place of acid, there were two additional peaks following chloroadamantane in glpc (column A). They were identified as 1-adamantanol and 2-adamantanone by peak enhancements in glpc (columns A and C) and infrared spectral comparison to authentic compounds. For example, from FeCl₃-AdH-SnCl₄ at 110° for 2.5 hr, 63% of

the adamantane was converted into a product mixture of the indicated composition: 1-chloroadamantane, 45%; 2-chloroadamantane, 7%; 1-adamantanol, 36%; and 2-adamantanone, 12%.

Isomerization of Chloroadamantanes. 1. Lower Temperatures.—In a 25 ml-flask, equipped with nitrogen inlet, magnetic stirrer, and condenser, 1 g (0.0059 mol) of 1-chloroadamantane was exposed to antimony pentachloride (1.76 g, 0.0059 mol) or ferric chloride (1.91 g, 0.0118 mol) in 12 ml of carbon tetrachloride at reflux. After work-up, product distribution was determined (Table II). Isomerizations were also carried out with aluminum chloride (0.784 g, 0.0059 mol) in 12 ml of 1,1,2-trichloro-1,2,2-trifluoroethane at room temperature (Table II).

2-Chloroadamantane was investigated similarly (Table II).

2. Higher Temperatures.—1-Chloroadamantane (1 g, 0.0059 mol) was treated with antimony pentachloride (1.76 g, 0.0059 mol) in stannic chloride at 110° or ferric chloride (1.91 g, 0.0118 mol) in titanium tetrachloride (12 ml) at 134° (Table III).

Adamantane and Ferric Chloride in *o*-Dichlorobenzene.—In a 100 ml, three-necked flask, furnished with nitrogen inlet, thermometer, mechanical stirrer, Friedrichs condenser, and hydrogen chloride trap, were placed 4.1 g (0.03 mol) of adamantane, 60 ml of *o*-dichlorobenzene, and 11.1 g (0.068 mol) of ferric chloride. The mixture was heated gradually during 90 min to 103°, at which temperature gas evolution became appreciable. After about 3 hr at 103°, since little gas was being evolved (88% total yield of hydrogen chloride), the reaction mixture was stirred with 200 ml of 1 *N* hydrochloric acid. The organic portion was washed twice with water, dried, and freed of solvent. The dark brown solid, 10.2 g, gave crystals, mp 115.8-116.8°, on repeated crystallization from benzene: *ir* (CS₂) for aromatic protons, 3.25 (lit.⁵⁸ for C-H stretch, 3.23-3.33), 11.50 (lit.⁵⁸ for isolated hydrogen, 11.11-11.63), 12.48 μ (lit.⁵⁸ for two adjacent hydrogens, 11.63-12.50); nmr (CCl₄) δ 1.6-2.0 (12 H), 2.09 (3 H), 7-7.5 (3 H), J_{ab} = 0.45, J_{bc} = 1.7 Hz (a = 3 position, b = 5, c = 6 in 1,2,4-trisubstituted benzene).

Anal. Calcd for C₁₆H₁₈Cl₂: C, 68.34; H, 6.45; Cl, 25.21. Found: C, 68.18; H, 6.32; Cl, 25.34.

With aluminum chloride (4.55 g, 0.034 mol) or water (0.3 ml, 0.0167 mol) as additives, about 1 hr was taken to reach the initiation temperature followed by 3.3-4 hr of heating at that temperature (Table V).

Commercial anhydrous ferric chloride (11.1 g) was further purified,⁵⁹ in relation to traces of water, by refluxing with 55 ml of carbon tetrachloride in a 100 ml, three-necked flask for 24 hr, and then distilling out the carbon tetrachloride. During the reflux, phosgene was flushed into a water trap. The apparatus was previously dried in the oven and protected from the water trap by a calcium chloride tube. Distilled *o*-dichlorobenzene (60 ml) was used, along with adamantane (4.1 g) dried over phosphorus pentoxide. The organic reaction components were handled with minimum exposure to air before addition to the purified ferric chloride (Table V).

Hydrogen chloride evolution was followed in each reaction.²

Chlorination with Molecular Chlorine.—Chlorine gas was bubbled through a mixture of adamantane (2.05 g, 0.015 mol) in 60 ml of stannic chloride for 5 min starting at 115°. During this period the temperature fell to 98-100°. After use of work-up procedure B, glpc analysis (column A) revealed an 8% yield of chloroadamantane, 1:2 molar ratio of 0.61.

Chlorination of Adamantane with *tert*-Butyl Chloride and Lewis Acid Catalyst. 1.—In a 100 ml, three-necked flask, equipped with nitrogen inlet, mechanical stirrer, Friedrichs condenser, thermometer, and constant-pressure addition funnel, a mixture of adamantane (4.1 g, 0.03 mol) and stannic chloride (60 ml) was heated at reflux. *tert*-Butyl chloride (2.78 g, 0.03 mol) was added dropwise during 2.5 min. After another 2.5-12.5 min. at 111 \pm 3°, the mixture was quenched with cold concentrated hydrochloric acid and extracted with carbon tetrachloride. Work-up procedure B and glpc (column A) gave chloroadamantane, 1:2 molar ratio \geq 1000:1.

2.—According to the procedure⁵⁸ of Gerzon and coworkers, a mixture of adamantane (10 g, 0.074 mol) and *tert*-butyl chloride (8.5 g, 0.092 mol) in 60 ml of cyclohexane was treated portionwise with aluminum chloride (1.05-1.35 g) at room temperature during 3-5 hr. Chloroadamantane, obtained in 64-74%

(58) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 1st ed, Wiley, New York, N. Y., 1964, p 60.

(59) M. E. Hill, *J. Org. Chem.*, **25**, 1115 (1960).

yield, generally displayed a 1:2 molar ratio of 20–50:1 (in one case, 275:1). Dichloroadamantane was formed in 4–8% yield.

Authentic Materials. 1-Chloroadamantane.—The procedure of Stetter,⁵¹ involving 1-adamantanol, gave a 96% yield of product, mp 162.5–163.5° (lit. mp 165°,^{21,54} 164.3–165.6°,⁵¹ 164–164.5°,⁵⁵ 159–160°,⁵⁶ 169–170°).⁵²

2-Chloroadamantane.—Adamantane on treatment with excess lithium aluminum hydride produced an 89% yield of crude 2-adamantanol^{60,61} which, on contact with phosphorus pentachloride,⁶² afforded crude 2-chloroadamantane (>99% yield). Glpc analysis, column A at 160°, showed the purity to be 96%, mp 190–191.8°, lit.⁶² mp 186–188° (both in sealed tubes), 192–193.5°.³⁵

1,3-Dichloroadamantane.⁵⁹—Adamantane (4.1 g, 0.03 mol) on exposure to aluminum chloride (4 g, 0.03 mol) at room temperature in carbon tetrachloride (60 ml) for 4 hr produced 1,3-dichloroadamantane in low yield. When half of the carbon tetrachloride was replaced with methylene chloride, after 10 min 1,3-dichloroadamantane was obtained in 49% yield, mp 131–131.5° (lit. mp 133°,⁶³ 132–134°,⁶⁴ 129.5–131.5°),⁶² in addition to an appreciable amount of chloroadamantane.

(60) P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961).

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(62) W. Hoek, J. Strating, and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **85**, 1045 (1966).

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(64) F. N. Stepanov and Yu I. Srebrodolskii, *Vestn. Kiev Politekhn. Inst., Ser. Khim.-Tekhnol.*, **2**, 6 (1967); *Chem. Abstr.*, **67**, 32355 (1967).

1-(1,2-Dichloro-4-phenyl)adamantane.—1-Bromadamantane (6.45 g, 0.03 mol) and ferric chloride (1.8 g, 0.011 mol) in *o*-dichlorobenzene (60 ml) at 78–82° for 1.6 hr gave dark brown, crude product which, on two crystallizations from benzene, gave white crystals, 3.75 g (44% yield), mp 115–115.3°. The infrared spectrum was essentially identical with the infrared spectrum of the product from adamantane–ferric chloride–*o*-dichlorobenzene.

When half of the *o*-dichlorobenzene was replaced by carbon tetrachloride, the reaction yielded the same aromatic product, along with chloroform, identified by glpc peak enhancement with columns C and D.

Registry No.—Adamantane, 281-23-2; ferric chloride, 7705-08-0; 1-chloroadamantane, 935-56-8; 2-chloroadamantane, 7346-41-0; *o*-dichlorobenzene, 95-50-1; antimony pentachloride, 7646-18-9.

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Synthesis of α, α -Dichlorosulfonyl Chlorides

W. GARY PHILLIPS* AND K. WAYNE RATTS

Monsanto Company, Agricultural Division, Research Department, St. Louis, Missouri 63166

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A general synthesis of stable α, α -dichlorosulfonyl chlorides from *S*-benzyl sulfides containing an active methylene group is presented. The mechanism of these chlorination reactions is discussed.

The synthesis of aryl sulfonyl halides by the treatment of certain aryl benzyl sulfides with sulfonyl chloride has been reported by Kharasch and Langford.¹ In this connection we wish to report a general facile



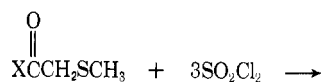
synthesis of stable, novel α, α -dichlorosulfonyl chlorides by the action of sulfonyl chloride on *S*-benzyl sulfides containing an active methylene group.

The general reaction for the synthesis of α, α -dichlorosulfonyl chlorides from β -keto sulfides is depicted in Scheme I.

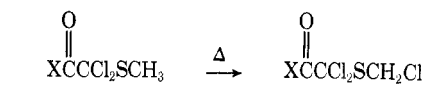
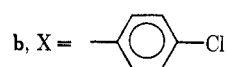
As can be seen in Table I, several α -carbamoyl *S*-benzyl sulfides gave dichlorosulfonyl chlorides in good yield. Chlorine was an adequate substitute for sulfonyl chloride. The products here were easily obtained in a pure state and were stable pale yellow to white solids. They were characterized by their elemental analysis and nmr spectra. Their nmr spectra are interesting in that they suggest a large barrier to rotation around the N–C bond; **2d** shows two septets for the methine protons separated by 1.4 ppm. Thus the carbonyl oxygen would be expected to be somewhat nucleophilic.

The preparation of α, α -dichlorosulfonyl halides is general in that **1g**, **1h**, and **1i** are also satisfactory. Unlike the α -carbamoyl sulfides, refluxing of these sulfides

in neat sulfonyl chloride was desirable to effect the cleavage. Also, unlike the α -carbamoyl sulfides, only *S*-benzyl sulfides were satisfactory; the *S*-methyl sulfides did not cleave but preferred to undergo further chlorination. Thus it appears that, if an SCH_3 group is employed, an amide function is necessary for the cleavage.

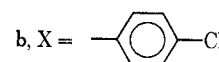
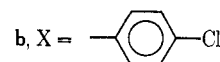


3a, X = $-\text{OC}_2\text{H}_5$



4a, X = $-\text{OC}_2\text{H}_5$

5a, X = $-\text{OC}_2\text{H}_5$



An α -chlorosulfonyl chloride is also formed when an aliphatic substituent is placed α to the carbonyl as in **6**. The expected product, **7**, was not formed but a high yield of **8** was obtained. Here the methyl group is monochlorinated in a unique β chlorination.

The β -carboxyl *S*-benzyl sulfides did not yield the expected α, α -dichlorosulfonyl chloride. When **9** was chlorinated the products were trichloromethylsulfonyl

(1) N. Kharasch and R. B. Langford, *J. Org. Chem.*, **28**, 1903 (1963).