Nuclear Magnetic Resonance Study of Alkyl Chloride Behavior in Aluminum Bromide–Chlorobenzene

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Received February 19, 1969

An nmr study of alkyl chlorides in the $AlBr_3$–chlorobenzene system at −50° provides evidence for the detection of a mobile *t*-amyl cation. The ion is involved in equilibria with the solvent leading to rapid scrambling of aromatic protons, and it may be cleanly trapped by hydride donors. Secondary cations are not detected in this system, but their presence as intermediates may be indirectly inferred from their reactions with hydride donors.

Aluminum bromide is a strong Lewis acid which has been extensively studied as a catalyst for paraffin isomerization and similar processes. These are thought to involve the formation of alkyl cationic intermediates which often rearrange and participate in facile hydride transfer reactions. Several years ago it was suggested that stable alkyl cations could be detected by nmr studies of alkyl halides in solutions containing antimony pentafluoride.[1] Tertiary cations are particularly easy to form and their spectra are characterized by substantial downfield shifts of groups α to the charged carbon.

In view of the large body of information about cations which have developed from these techniques it is somewhat surprising that nmr has been scarcely applied to the study of the aluminum bromide system. In 1967 it was reported that solutions of aluminum bromide in 1,2,4-trichlorobenzene could initiate and support extremely long chain hydride transfer processes between isobutane and low concentrations of *t*-butyl cations.[2] The rapid intermolecular hydride transfer reaction collapses the methyl doublet in isobutane's nmr spectrum, but since the ion concentration is low there is no detectable shift in its position. The nmr spectrum of 1,2,4-trichlorobenzene is nearly unchanged while the hydride exchange is occurring so that, if any proton exchange with solvent is going on simultaneously, it must be relatively slow. To a first approximation it thus appears that cation interaction with the solvent is small and one might hope to ionize a sufficient amount of *t*-butyl chloride in $AlBr_3$–1,2,4 trichlorobenzene to be detected by nmr. However, it has been our experience that *t*-butyl chloride does not simply ionize but at ambient conditions eliminates HCl and forms isobutylene which reacts *via* a myriad of paths as in sulfuric acid,[3] to produce a complex nmr spectrum, presumably of allyl ions. One doesn't know whether the elimination of HCl reflects an inherently lower acidity of the HCl–$AlBr_3$ system compared with HF–SbF_5 or if 1,2,4-trichlorobenzene is simply too basic a solvent with which to confine the latently reactive *t*-butyl cation. Unfortunately, trichlorobenzene freezes at 17° and, although supercooled solutions can be prepared, it is inconvenient for studies at low temperatures.

A number of potentially useful solvents have been investigated for their compatibility with *t*-alkyl ions and aluminum bromide at low temperatures. This report deals with the chlorobenzene–aluminum bromide system, a more basic medium then 1,2,4-trichlorobenzene which however can be used at −50° and which supports a limited range of cationic reactivity. The nmr spectra to be discussed are not so easily related to the presence of "stable" cations as are those obtained with SbF_5, but their detection seems plausible when the spectra are considered with the results of hydride transfer trapping experiments.

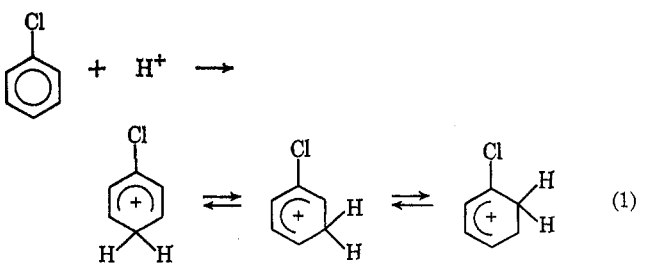
Experimental Section

Half molar solutions of redistilled aluminum bromide in chlorobenzene dried with barium oxide or 13-X molecular sieves were used throughout. At −50° the nmr spectra of these solutions were the same as that of neat chlorobenzene. At room temperature, however, the solvent's spectrum was partially collapsed, probably owing to trace amounts of moisture in the aluminum bromide. The background exchange could be stopped by adding small amounts of more basic hydrocarbons such as mesitylene to the system but neither repeated distillation of $AlBr_3$ nor the use of sublimed $AlBr_3$ eliminated this reactivity.

Alkyl halides were added to these solutions at or below the temperature of the nmr scan. Carbonium ion intermediates were conveniently trapped by adding hydride donors, paraffins, or naphthenes to the nmr tubes and shaking vigorously for a few seconds at reaction temperature. The nmr spectra of the resulting solutions, could be examined and the products recovered by vacuum distillation for gas chromatographic analysis.

Results and Discussion

The 60-Mc nmr spectrum of chlorobenzene is complex and exhibits considerable fine structure.[4] The spectrum while unaffected by the presence of $AlBr_3$ at −50° may be collapsed by the subsequent addition of catalytic quantities of HCl or HBr, Figure 1. The change in the spectrum is indicative of the existence of an exchange process resulting in the rapid equilibration of all solvent protons. Such a process probably involves both intra- and intermolecular proton migration, eq 1 and 2. At high rates of exchange the spectrum is a



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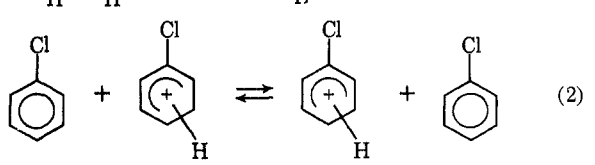


(2)

(1) (a) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Amer. Chem. Soc.*, **85**, 1328 (1963); (b) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360 (1964).

(2) G. M. Kramer, B. E. Hudson, and M. T. Melchior, *J. Phys. Chem.*, **71**, 1525 (1967).

(3) N. Deno, H. G. Richey, Jr., J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **85**, 2991 (1963).

(4) S. Castellano, R. Kostelnik, and C. Sun, *Tetrahedron Lett.*, 4635 (1967).

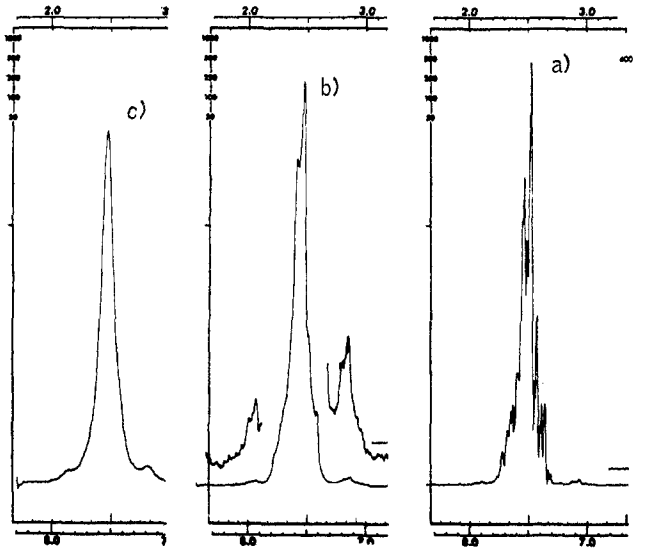
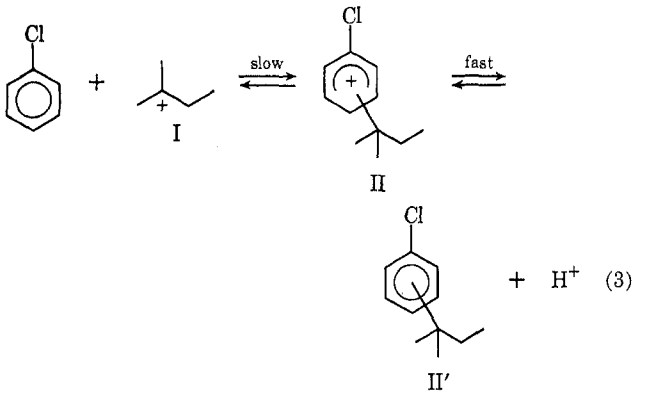


Figure 1.—The spectrum of chlorobenzene-containing 0.5 M $AlBr_3$ at −50°: (a) neat; (b) +0.02 M HCl; (c) +0.2 M HCl.



enough on nmr time scale to permit the apparent observation of ions I and II, the latter in rapid equilibrium with an undetermined amount of amyl chlorobenzenes.

The spectrum of 0.2 M t-amyl chloride in the 0.5 M $AlBr_3$–chlorobenzene solution at −50° is characterized by a multicomponent peak centered at −0.88 ppm, a singlet at −2.63 ppm, and a broad peak at −3.57 ppm

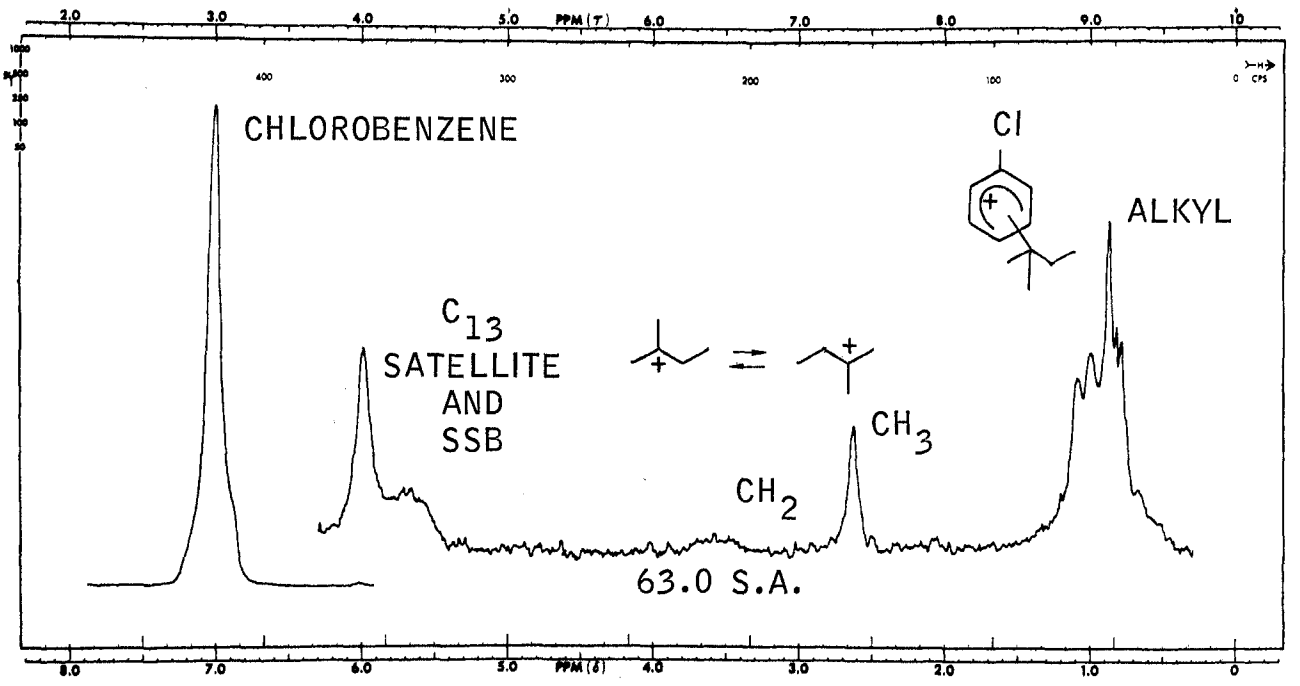
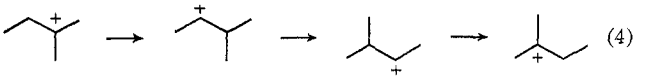


Figure 2.—The spectrum of 0.16 M t-$C_5H_{11}Cl$ in chlorobenzene-containing 0.5 M $AlBr_3$, at −50°.

singlet centered at −7.00 ± 0.02 ppm (referred to TMS as an internal reference). The lifetime of solvent molecules under these conditions ought to be between 0.01 and 0.1 sec. Unfortunately, we do not have the means of quantitatively evaluating the exchange rates and energetic parameters from the spectral data.

A similar collapse of the solvent spectrum is caused by the addition of t-butyl, t-amyl, or isopropyl chloride or bromide. This indicates that the halides form cations which either add to or protonate chlorobenzene thus initiating the exchange. At this time the spectrum of the alkyl halide is immediately altered. The tertiary halides yield a number of bands which are most easily interpreted in terms of an equilibrium between tertiary cations + solvent and the alkylated solvent, eq 3. The equilibrium is attained rapidly, but slowly (Figure 2). The singlet at −2.63 ppm and the broad band at −3.57 ppm are assigned to the t-amyl cation undergoing rapid equilibration of the methyl groups, possibly by intramolecular hydride and methide shifts (eq 4). These shifts lead to the time-averaged


(4)

equilibration of all methyl groups in the ion and are responsible for the −2.67-ppm singlet. Such an explanation has been proposed by Olah to account for the coalescence of the separate methyl resonances of the stable cation upon heating to +90° in HSO_3F–SbF_5,[5]

(5) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227 (1967).

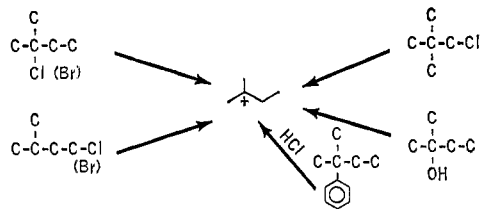


Figure 3.—Precursors forming the *t*-amyl cation.

the results of trapping with many hydride donors and the ease with which it is obtained from many precursors.

The −2.63-ppm peak contains about 10% of the combined area of the −0.88, −2.63, and −3.57 peaks. The peak area is proportional to the *t*-amyl chloride concentration up to an RCl:$AlBr_3$ ratio of 0.4:1 but falls off at much higher values, possibly because of a

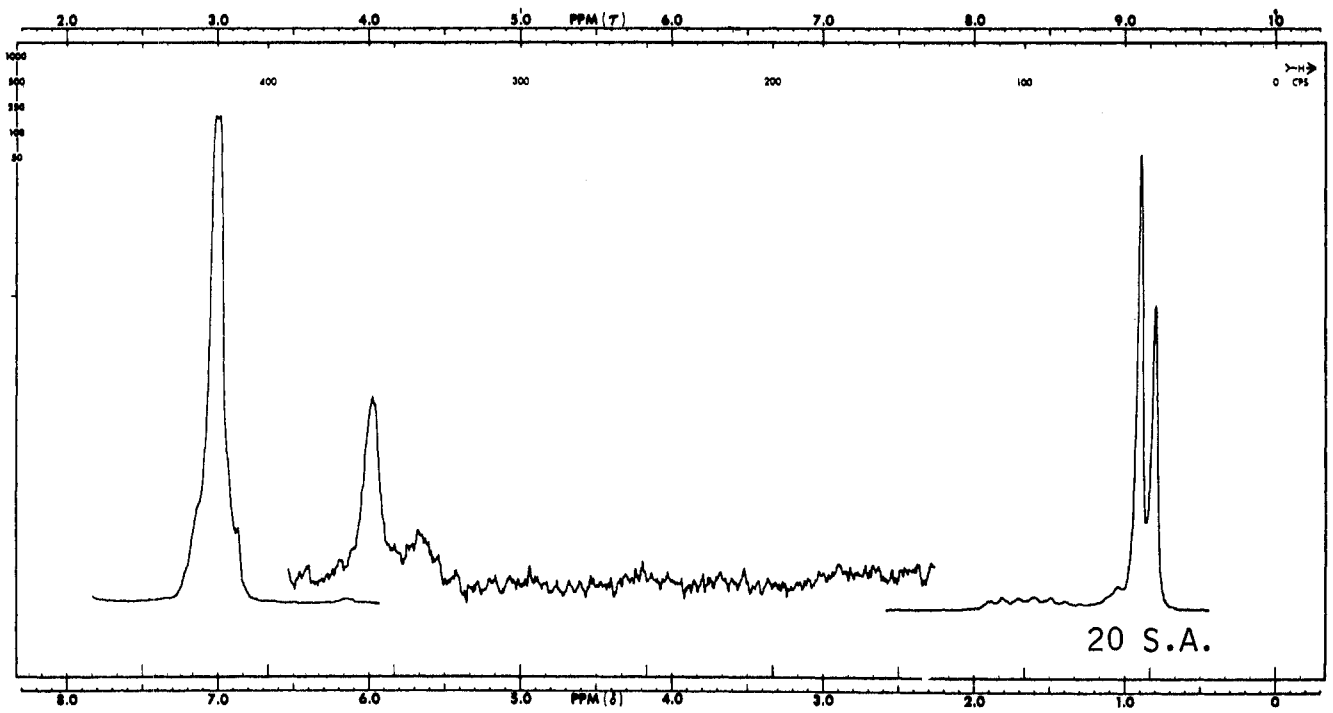


Figure 4.—The spectrum of isobutane after reacting with 0.16 *M* *t*-$C_5H_{11}Cl_3$, −50° (*i*-C_4H_{10}:*t*-$C_5H_{11}Cl$ = 25:1). Isobutane's spectrum is broadened owing to intermolecular hydride transfer, *i*-C_4H_{10} + *t*-$C_4H_9^+ \rightleftharpoons$ *t*-$C_4H_9^+$ + *i*-C_4H_{10}.

or at much lower temperatures in SbF_5–SO_2FCl solution.[1b] With SbF_5 the position of the collapsed methyl peak is at −3.60 ppm, 1 ppm further downfield than in chlorobenzene. The peak position probably is due to several factors, namely that the ion may exist in equilibrium with small concentrations of alkyl chlorides, bromides, or amylenes and it may also be subject to specific solvation by chlorobenzene, a factor often leading to upfield chemical shifts.[6] In any case the spectrum indicates that the *t*-amyl cation is a major component of these equilibria.

The band at −3.57 ppm is assigned to the methylene protons. Saunders has shown that the CH_2 band in the SbF_5–SO_2FCl system contains extensive fine structure,[7] which is lost in SbF_5–HSO_3F and hardly apparent in $AlBr_3$–chlorobenzene. The fine structure has been taken as evidence that rearrangements of the *t*-amyl cation in SbF_5–SO_2FCl involve strictly intramolecular processes. If intermolecular proton exchange were to occur rapidly, coupling to the CH_2 group would be reduced and ultimately eliminated. The broad CH_2 band in $AlBr_3$–chlorobenzene thus suggests that proton exchange occurs at modest rates in this system.

Evidence that the spectrum is probably that of the *t*-amyl ion comes not only from the nmr but also from

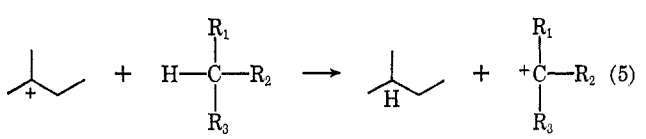
(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Inc., New York, N. Y., 1959, p 427.

(7) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968).

change in stability of the ionic complexes from those initially involving dimeric aluminum bromide to those with the monomer.

Spectra equivalent to that obtained with *t*-amyl chloride have been obtained with 1-chloro-3-methylbutane, 1-chloro-2,2-dimethylpropane, *t*-amyl alcohol, *t*-amylbenzene + HCl, and similar compounds (Figure 3). 1-Chloropentane and 2-chloropentane do not appear to isomerize to the tertiary ion. In this respect the system differs from neat SbF_5 which permits a ready isomerization of the secondary cations.

The −2.63-ppm peak is immediately removed from the spectrum by shaking the nmr tube with an excess of a tertiary hydride donor at −50°, eq 5. The resulting



(5)

spectrum is then essentially that of the donor rapidly transferring hydride ions to a small concentration of skeletally similar ions. When the donor is isobutane this process may broaden and coalesce its doublet to a singlet.[2] Vacuum distillation from the sample tube leads to a clean recovery of isopentane. While yields are somewhat biased in favor of the light component by this procedure the recovery of isopentane is approxi-

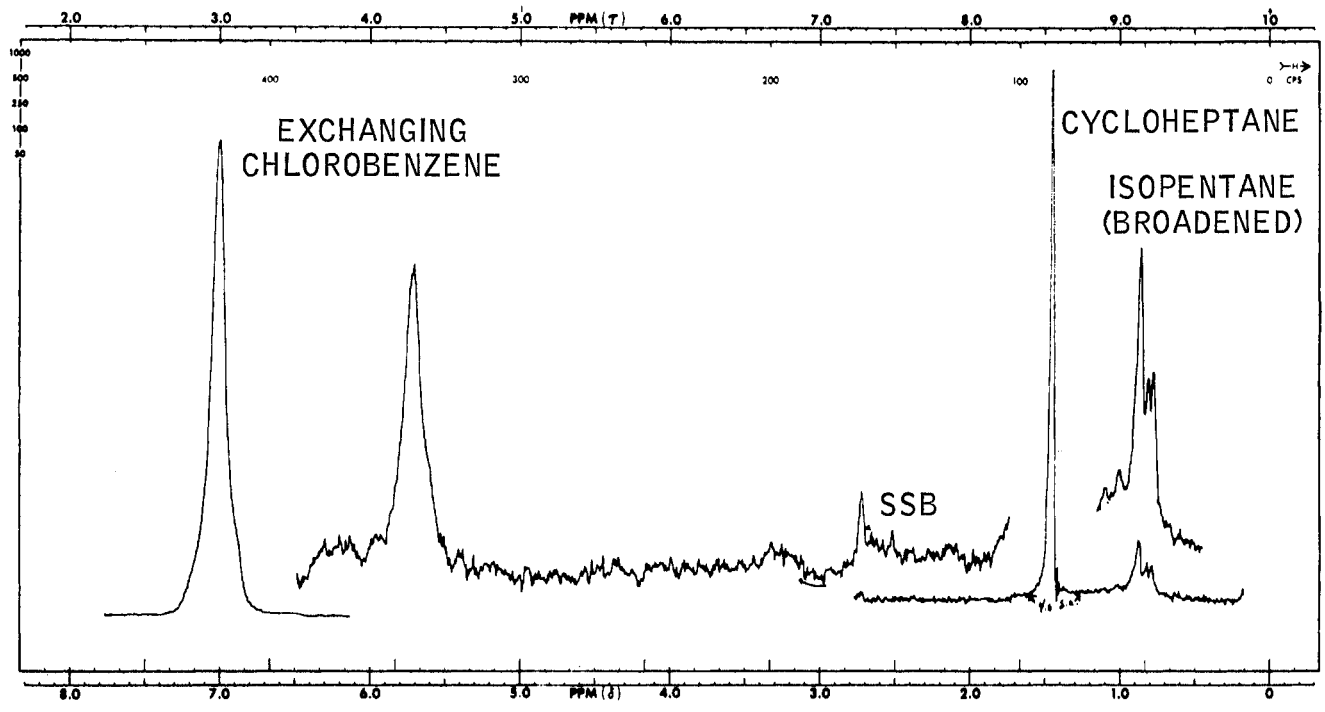


Figure 5.—Isopentane is trapped by reaction of 0.16 *M* *t*-$C_5H_{11}Cl$ in 0.5 *M* $AlBr_3$–chlorobenzene with cycloheptane at 50° (cycloheptane: *t*-amyl chloride = 25:1).

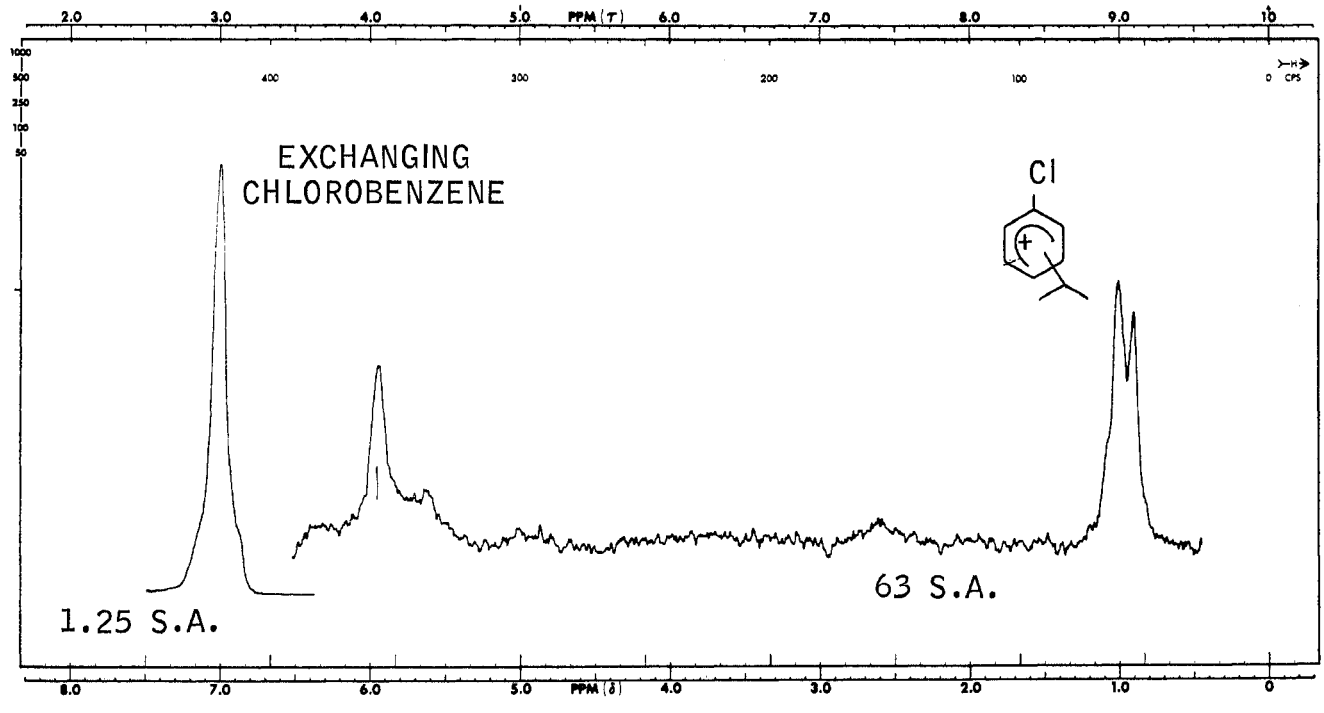


Figure 6.—The spectrum of 0.16 *M* *i*-C_3H_7Cl in 0.5 *M* $AlBr_3$–chlorobenzene, −50°.

mately quantitive. Similar experiments have been carried out with 2,3-dimethylbutane, 2,2,3-trimethylbutane, and methylcyclopentane as donors. The nmr spectrum of a typical reaction with isobutane is shown in Figure 4.

The −2.63-ppm peak is also destroyed upon reaction with secondary hydride donors such as *n*-hexane, cycloheptane, and cyclooctane at −50°. Isopentane is again recovered but the nmr spectra of these compounds does not undergo much change. This would be consistent with hydride transfer from secondary sources being slow on the nmr time scale but fast enough to reduce the half-life of the *t*-amyl cation to less than several minutes. Rearrangement of the secondary donors is slow at −50° but isomerization of the naphthenes can be detected.

The isopentane formed by reaction with cycloheptane appears to participate in rapid hydride transfer with a small concentration of residual *t*-amyl cations, thus broadening its spectrum (Figure 5). Cycloheptane's nmr spectrum remains a single sharp line while this occurs. A corresponding experiment with cyclooctane leads to isomerization of the naphthene and interference with isopentane's spectrum.

The nmr spectrum of *t*-butyl chloride is a singlet at −1.4 ppm. In the $AlBr_3$–chlorobenzene system at −50°, 0.2 *M* solutions of *t*-butyl chloride exhibit a very small peak at −4.1 ppm which may be the cation and a closely spaced pair of peaks at −0.98 ppm with a spacing of 2–3 cps. The small peak diminishes as the temperature is raised, is not visible at −10°, but reappears upon cooling to −30. The upfield peaks also undergo a reversible change in relative intensity with temperature. *t*-Butyl bromide under similar conditions yields only one upfield peak.

The small and rather broad peak at −4.1 ppm suggests that the *t*-butyl cation is undergoing proton exchange with HX or the solvent. There is no simple explanation for the different spectral behavior of *t*-butyl chloride and bromide but the spectra may be readily obtained from isobutyl halides or *t*-butyl benzene + HX and isobutane is cleanly recovered from any of the systems by reaction with hydride donors. The spectra are not obtained with the normal butyl halides.

While the nmr study of tertiary cation sources in $AlBr_3$–chlorobenzene provides some evidence for the presence of relatively stable ions, no indication of stable secondary ions has been found by similar means. Isopropyl chloride's spectrum is, however, immediately altered in this system (Figure 6). The methyl doublet shifts upfield and broadens noticeably and the methine proton's septet also moves upfield and broadens. The same spectrum is obtained with 1-chloropropane and there is no evidence of low field peaks attributed to the isopropyl cation.[1b]

On the other hand, chlorobenzene's spectrum collapses to a singlet indicating the formation of an alkyl aromatic cation like III. Attempts to trap propyl cations by hydride transfer from methylcyclopentane lead to the formation of only small amounts of propane, 1 to 5% of theory. Again, small yields of propane are obtained if the alkyl cations are generated by the addition of HCl to isopropylbenzene. Isopropylbenzene rapidly reacts, however by, transferring the alkyl group to chlorobenzene generating the 3 isopropyl chlorobenzenes.[8]

The behavior of isopropyl chloride and cumene leads to the conclusion that the nmr spectrum is probably that of a system conatining mainly protonated isopropyl chlorobenzenes. The isopropyl groups are considered to be involved in rapid disproportionation reactions between solvent molecules. Broadening of the alkyl protons is attributed both to the alkyl exchange which interconverts *ortho*, *meta*, and *para* isomers and to reversible protonation of the alkylchlorobenzenes which rapidly alters the environment of the alkyl group.

We do not understand why the addition of methylcyclopentane to protonated isopropyl chlorobenzene should only yield small quantities of propane. If the ion III were in rapid equilibrium with chlorobenzene and an isopropyl cation, quantitative recovery of propane might be anticipated. A possible explanation has been tendered by our colleagues, namely that III is in resonance with IIIa and may contain a proton of sufficient acidity to abstract hydride from methylcyclopentane. If this reaction was fast while ionization was slow it could account for our results, but this possibility has not been investigated.

(8) Determined by gas chromatography and mass spectroscopy after quenching the system in water.

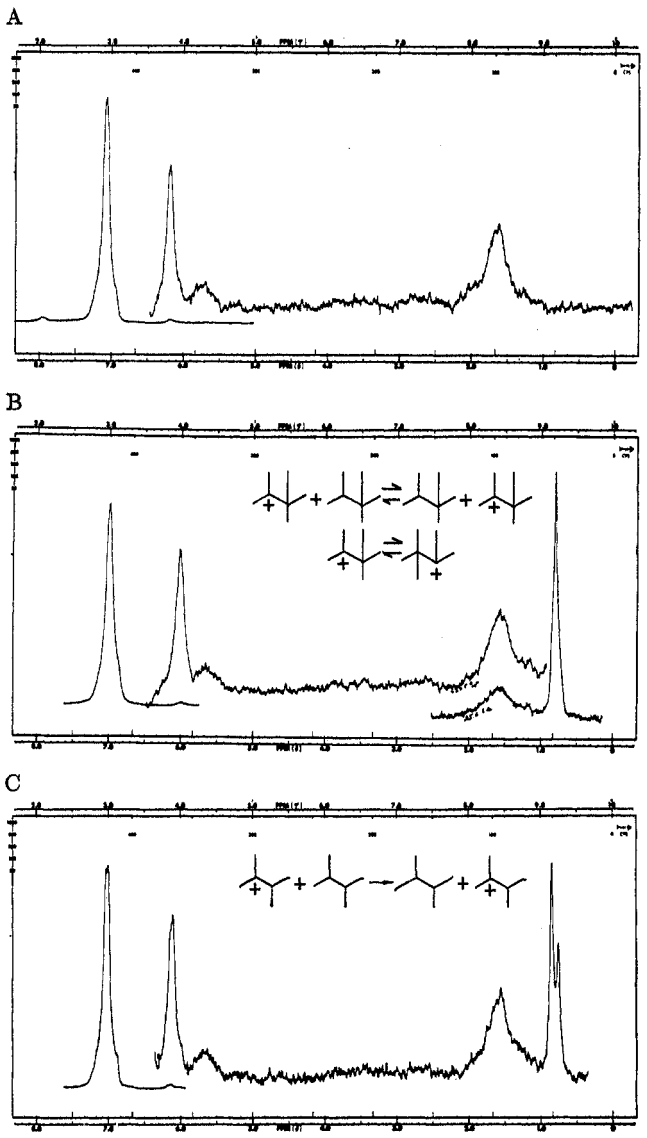
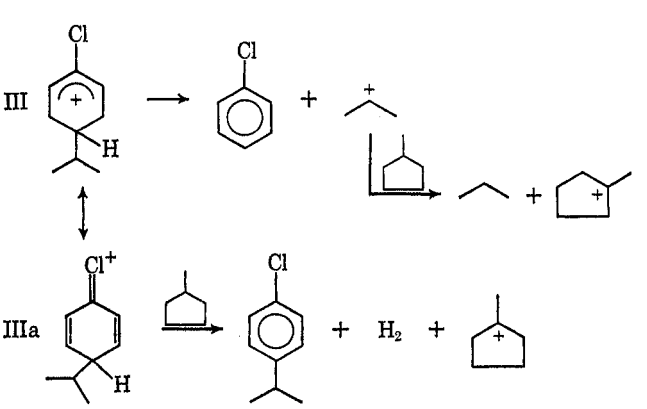


Figure 7.—The spectrum of 0.16 *M* bromocyclopentane in 0.5 *M* $AlBr_3$–chlorobenzene at −50°: (A) alone; (B) 0.1 *M* 2,2,3-trimethylbutane added; (C) 0.1 *M* 2,3-dimethylbutane added.



Although isopropyl chloride does not form a stable secondary ion the formation of some propane indicates their presence as reactive intermediates. Other secondary sources such as cyclopentyl and cyclohexyl

halides also react with tertiary hydride donors. The nmr spectrum of the cyclic halide is but slightly affected as the reaction appears to generate tertiary ions which initiate hydride transfer chain reactions with the remaining donor molecules. For example, reaction with 2,2,3-trimethylbutane and 2,3-dimethylbutane leads to immediate exchange broadening of the paraffins spectra (Figure 7). The spectra indicate that methyl migration is rapid in the former system. These halides also initiate the rearrangements of cycloheptane or cyclooctane which however occur slowly at −50°.

Thus in the $AlBr_3$–chlorobenzene system hydride transfer from tertiary or secondary sources to tertiary or secondary cations has been observed at quite low temperatures. Spectra of solutions of tertiary halides contain bands consistent with the presence of tertiary cations. The bands may be removed by reaction with hydride donors and hydrocarbons of the proper structures cleanly recovered. High field nmr bands are also present which suggest the presence of protonated alkyl aromatics.

Registry No.—Chlorobenzene, 108-90-7; *t*-amyl chloride, 594-36-5; isobutane, 75-28-5; cycloheptane, 291-64-5; *t*-butyl chloride, 507-20-0; isopropyl chloride, 75-29-6; bromocyclopentane, 137-43-9.

The Formation of Sulfur–Sulfur Bonds by the Chloramination of Thiols[1]

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Received September 28, 1969

Chloramine and dimethylchloramine react with cyclohexylmercaptan, thiophenol, 2-mercaptonaphthalene, 2-mercaptopyridine, 2-mercaptoethanol, 1-butanethiol, and 1,2-ethanedithiol with the extraction of the thiol hydrogen atoms and the formation of sulfur–sulfur bonds. There is an indication that the first step in the reaction is the formation of compounds of the type $RSNH_2$ or $RSN(CH_3)_2$. Possible mechanisms for the chloramination reactions are discussed.

It has been well established that the chloramine molecule reacts with electron-donor molecules in accordance with the equation

$$B: + NH_2Cl \longrightarrow [B:NH_2^+]Cl^-$$

where B: is the Lewis base. Among the Lewis bases studied are those containing nitrogen, phosphorus, arsenic, or antimony atoms as the basic centers of the molecule. During the past decade, the reactions of chloramines of the type $R_2'NCl$, where R′ = H or alkyl, with amines, phosphines, arsines, and stibines have been extensively investigated in this laboratory.[2-13]

We were interested in studying the reactions of chloramines with compounds in which sulfur is the electron-donor atom. We hoped that such reactions of $R_2'NCl$ (R′ = H or alkyl) with thiols would result in the cleavage of the N–Cl bonds in the chloramine molecules with the formation of sulfenamides of the types $RSNH_2$ and $RSN(CH_3)_2$. Previous work reported in the literature indicating that aqueous solutions of chloramine react with alkali metal mercaptides to yield insoluble sulfenamides[14-18] supported this suggestion. In all these cases, ammonia was present in excess.

It was our thinking that formation of the disulfide is the initial step in these reactions and that the sulfenamide is obtained by the cleavage of RS–SR to $RSNH_2$ and RSCl followed by the formation of a second molecule of $RSNH_2$ by ammonolysis of RSCl. This thinking was based on the reported formation of disulfides by oxidation (by means other than chloramination) of thiols.[19]

Therefore, when we observed that cyclohexylmercaptan reacts with dimethylchloramine in ethereal solution to give dicyclohexyl disulfide in good yield, we decided to investigate the series of reactions to determine if the sulfenamides, as well as the disulfides, could be obtained and under what conditions. We were also interested in the possibility of forming $[RSN]_n$ polymers.

Carr and coworkers[15] had found the presence of some disulfides in their oxidation of mercaptides to sulfenamides in aqueous media and had speculated concerning the mechanism of the reactions.

The results of the research we report here show that the disulfide is obtained almost exclusively from the chloramination of thiols in ethereal solution with either chloramine or dimethylchloramine. The presence of ammonia in the reactions with chloramine does not change the result. The results indicate the probability

(1) (a) This research was reported at the 22nd meeting-in-miniature of the Florida Section of the American Chemical Society, Jacksonville, Fla., May 1969.

(2) (a) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Amer. Chem. Soc.*, **81**, 2982 (1959). (b) W. A. Hart and H. H. Sisler, *Inorg. Chem.*, **3**, 617 (1964).

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