The Hofmann Elimination of Trimethyl-1,2,2-triphenylethylammonium-1-C^{14} Hydroxide

WILLIAM A. BONNER[1] AND FREDERIC J. KAKIS

Department of Chemistry, Stanford University, Stanford, California

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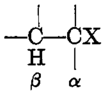
Trimethyl-1,2,2-triphenylethylammonium-1-C^{14} hydroxide (XI, 0.737 mc./mole) was synthesized and pyrolyzed under the conditions of the Hofmann elimination, affording triphenylethylene-C^{14} as the sole product. Oxidative degradation of the latter, followed by radioactivity assay of the fragments, disclosed that virtually all of the label resided in the benzoic acid (α-C) fragment, and that less than 0.4% was present in the benzophenone (β-C) fragment. Thus, the pyrolysis of XI occurred without significant skeletal rearrangement. In view of the extreme ease with which the 1,2,2-triphenylethyl carbonium ion has been shown previously in other reactions to suffer rearrangement, we exclude the mechanistic involvement of such an intermediate, either of the classical or nonclassical type, in the present elimination. The results are consistent, however, with a synchronous E2 or an E1cb mechanism.

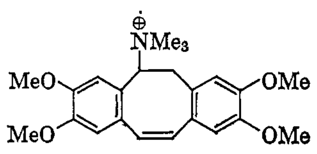
The principal β-elimination reaction mechanisms,[2] E1, E2, and E1cb, differ in the temporal sequence in which the α-C–X and the β-C–H bonds in the system



$$\underset{\beta}{-\overset{|}{\underset{\text{H}}{\text{C}}}}-\underset{\alpha}{\overset{|}{\underset{|}{\text{C}}}}\text{X}$$

are ruptured. In E2 eliminations scission of both bonds occurs simultaneously, but presumably may proceed at different rates for each bond. It is thus now appreciated[3,4] that concerted E2 eliminations need not be uniformly synchronous and that structural and environmental factors may dictate that such eliminations proceed *via* transition states which vary from the carbonium ion to the carbanion extreme of the mechanistic spectrum. The critical studies providing evidence for such wide departures from the conventional E2 picture have been summarized and evaluated by Bunnett,[4] who also has examined the factors influencing the nature of the transition state of a given β-elimination reaction and its position between the "nearly E1" and "nearly carbanion" extremes in the spectrum of E2 elimination mechanisms.

The mechanistic data available for the decomposition of quaternary ammonium compounds are less extensive than those for eliminations involving alkyl halides, tosylates, alcohols, and the like. The most common mechanism for Hofmann eliminations appears to be the E2 type.[2,5,6] However, the majority of Hofmann elimination studies have not involved molecules of more complex structures, where departures from the conventional E2 picture might be anticipated. Thus, while the intervention of an E1 mechanism in Hofmann eliminations is rather uncommon, carbonium ions have been postulated in several Hofmann eliminations where electronic or steric factors may favor their formation. Quaternary derivatives such as I,[7,8] II,[9] III,[10] IV,[11] and related compounds, for example, whose E1 decomposition might lead to a resonance-stabilized benzyl-type cation, have been postulated to react *via* carbonium ion intermediates. Regarding steric factors, it has been found that the neomenthyltrimethylammonium ion (V) decomposed to 3-menthene (VI),[12] a Saytzeff product, and that the *cis*-2-methylcyclohexyltrimethylammonium ion (VII) likewise gave



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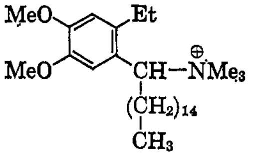

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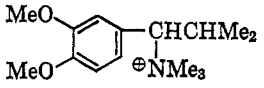

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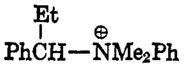
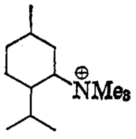
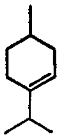


$$\text{Ph}\overset{\text{Et}}{\overset{|}{\text{C}}}\text{H}-\overset{\oplus}{\text{N}}\text{Me}_2\text{Ph}$$

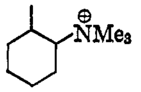
IV



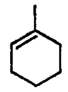
V



VI



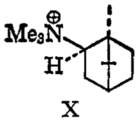
VII



VIII

primarily the Saytzeff product VIII.[13] These results have been explained[4] in terms of steric compression of the bulky $\text{Me}_3\text{N}^{\oplus}$– group against the cyclohexane framework, a factor which provides a driving force for its E1 ejection, despite the fact that β-hydrogens are available in the *trans*-coplanar orientation presumably favorable[14] to E2 elimination. An example of a Wagner–Meerwein rearrangement during Hofmann elimination is provided in the work of McKenna and Slinger,[15] who isolated (+)-camphene (IX) from the decomposition of the trimethyl-(−)-neobornylammonium ion (X). The rate of this elimination proved independent of the concentration of the base, a result consistent with the E1 picture. The several examples

IX



X

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[1] To whom correspondence should be sent.

[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VIII.

[3] C. K. Ingold, *Proc. Chem. Soc.*, 265 (1962).

[4] J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, **1**, 225 (1962).

[5] D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 314.

[6] V. J. Shiner, Jr., and M. L. Smith, *J. Am. Chem. Soc.*, **80**, 4095 (1958).

[7] A. R. Battersby and R. Binks, *J. Chem. Soc.*, 2888 (1955).

[8] A. R. Battersby and H. T. Openshaw, *ibid.*, S59 (1949).

[9] M. Pailer and L. Bilek, *Monatsh.*, **79**, 135 (1948).

[10] G. Norcross and H. T. Openshaw, *J. Chem. Soc.*, 1174 (1949).

[11] D. A. Archer and H. Booth, *Chem. Ind.* (London), 1570 (1962).

[12] E. D. Hughes and J. Wiley, *J. Chem. Soc.*, 4094 (1960).

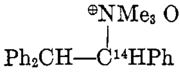
[13] T. H. Brownlee and W. H. Saunders, Jr., *Proc. Chem. Soc.*, 314 (1961).

[14] Reference 2, p. 467.

[15] J. McKenna and J. B. Slinger, *J. Chem. Soc.*, 2759 (1958).

above illustrate the type of system wherein steric or electronic features lead to variations in the usual E2 mechanism for Hofmann elimination.

In the present investigation we have, for several reasons, selected trimethyl-1,2,2-triphenylethylammonium-1-C^{14} hydroxide (XI) as a model compound

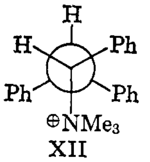


$$\underset{\text{Ph}_2\text{CH—C}^{14}\text{HPh}}{\overset{\oplus\text{NMe}_3\ \text{OH}^{\ominus}}{|}}$$

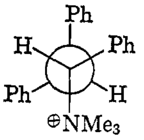
XI

with which to study the Hofmann elimination. First, numerous other solvolysis and elimination reactions in the 1,2,2-triphenylethyl system have been studied extensively from a mechanistic viewpoint.[16–23] Thus, the behavior of some of the intermediates through which the elimination might proceed would, to that extent, be predictable. Second, the use of a C^{14} label at α-C in XI should permit the detection of certain of these intermediates, by analogy with previous studies.[16–23] Third, as enumerated below, XI has structural features which for steric and electronic reasons might be anticipated to influence the mechanism of the elimination in opposing directions.

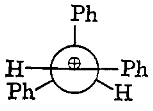
The phenyl substituent at α-C in XI, for example, should shift the mechanism toward the "E1-like" end of the E2 elimination spectrum.[4] The ultimate possibility of a fully E1 process is also reasonable, owing to the resonance stabilization which is possible for the benzyl-type carbonium ion thus produced.[7–11] Alternatively, the inductive effect of the $Me_3N^{\oplus}$– group at α-C, as well as the two phenyl groups at β-C, activating the β-hydrogen in XI, should favor a transition state toward the carbanion end of the elimination spectrum.[4] Again, a fully developed E1cb mechanism is theoretically possible, owing to effective resonance stabilization for the β-C carbanion thus involved, as well as the resulting relief of steric compression[24] at β-C. In addition, conformational and steric features in XI are such that deviations from a fully synchronous elimination appear possible. Thus, molecular models of XI reveal severe steric interactions between the β-C phenyl groups and the bulky $Me_3N^{\oplus}$– function at α-C. These repulsions do not appear to be substantially relieved during rotation about the α-C–β-C bond, and they are most severe in the conformation XII, which places the β-C–H and the α-C $Me_3N^{\oplus}$– groups in the *trans*-coplanar orientation most favorable for E2 elimination. Reaction from the slightly less constricted conformation XIII, on the other hand, might be expected to proceed by the E1 path, with steric compression substantially reduced by expulsion of the $Me_3N^{\oplus}$– group and formation of the open 1,2,2-triphenylethyl carbonium ion XIV. Furthermore, conformation XIII bears a phenyl group at β-C, which is strategically situated to engage in neighboring-group participation in the $Me_3N^{\oplus}$ expulsion, such that the rearranged but sterically equivalent carbonium ion XV might also be expected during E1 elimination. Such phenyl participation might appear advantageous here, since it would provide a transition state wherein the positive charge could be more effectively delocalized, and in addition would permit a mechanism for relief of steric compression (B strain) at β-C. The formation of nonclassical, bridged, cationic intermediates also cannot be excluded *a priori*, despite the complete lack of evidence for them so far in other reactions of the 1,2,2-triphenylethyl system.[18–20,22] Finally, there is no theoretical reason precluding a fully synchronous E2 elimination as the mechanism open to XI.



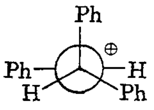
XII



XIII



XIV



XV

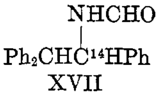
It was hoped to distinguish between some of the above alternatives by means of the C^{14} label at α-C in XI. In view of the known statistical redistribution of phenyl groups during the lifetime of the 1,2,2-triphenylethyl carbonium ion,[16–23] label randomization approaching, but not exceeding, 50% during Hofmann elimination of XI would be indicative of a simple E1 mechanism. Phenyl migration exceeding 50%, on the other hand, would suggest an E1 mechanism aided by neighboring-group participation. A fully concerted E2 mechanism by contrast should permit no phenyl redistribution, a result also arising from a simple E1cb path. The extent to which phenyl migration might occur during an E2 mechanism with a "nearly E1" transition state[4] appears at this stage to be not predictable. The possible existence of nonclassical ionic intermediates within an E1 framework, however, could be readily evaluated, if necessary, by the double-labeling techniques previously employed in the 1,2,2-triphenylethyl system.[18,19]

Results

The radioactive quaternary base XI was synthesized by the following sequence of reactions. Phenyl benzhydryl ketone-carbonyl-C^{14} (XVI) was prepared as previously described.[16] The ketone was subjected to the

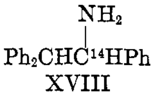
$Ph_2CHC^{14}OPh$

XVI



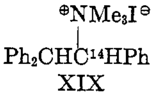
$$\overset{\text{NHCHO}}{\underset{}{}}\;\text{Ph}_2\text{CH}\overset{|}{\text{C}}{}^{14}\text{HPh}$$

XVII



$$\overset{\text{NH}_2}{\underset{}{}}\;\text{Ph}_2\text{CH}\overset{|}{\text{C}}{}^{14}\text{HPh}$$

XVIII



$$\overset{\oplus\text{NMe}_3\text{I}^{\ominus}}{\underset{}{}}\;\text{Ph}_2\text{CH}\overset{|}{\text{C}}{}^{14}\text{HPh}$$

XIX

Leuckart reductive amination by employing a mixture of 99% formamide and 90% formic acid containing magnesium chloride catalyst, affording N-formyl-1,2,2-triphenylamine-1-C^{14} (XVII). Subsequent hydrolysis of the latter provided a more suitable over-all preparation of the desired radioactive amine XVIII than did the previously employed[20] reduction of the oxime of XVI. The conversion of XVIII to the quaternary iodide XIX proved possible only under drastic conditions and was accomplished by extensive heating of XVIII with excess methyl iodide and aqueous

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(16) W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, **75**, 5372 (1953).

(17) C. J. Collins and W. A. Bonner, *ibid.*, **75**, 5379 (1953).

(18) C. J. Collins and W. A. Bonner, *ibid.*, **77**, 92 (1955).

(19) W. A. Bonner and C. J. Collins, *ibid.*, **77**, 99 (1955).

(20) W. A. Bonner and C. J. Collins, *ibid.*, **78**, 5587 (1956).

(21) W. A. Bonner, *ibid.*, **81**, 1181 (1959).

(22) C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959).

(23) W. A. Bonner and T. A. Putkey, *J. Org. Chem.*, **27**, 2348 (1962).

(24) F. G. Bordwell, R. L. Arnold, and J. B. Biranowski, *ibid.*, **28**, 2496 (1963).

sodium carbonate in a stainless steel bomb. This difficulty in quaternizing XVIII is, we believe, indicative of the above discussed steric compressions inherent in the quaternary cation of XIX. Preparation of the base XI from the iodide XIX was achieved in aqueous solution using an ion-exchange column, and Hofmann elimination of XI was performed *in situ* by distillation and pyrolysis of the residue at 194°. The radioactive triphenylethylene product was subsequently oxidatively cleaved[16] into benzophenone and benzoic acid, and these were assayed for radioactivity to determine the label distribution in their triphenylethylene precursor. Virtually all of the label was found to reside in the benzoic acid fragment (from α-C of XI), and less than 0.4% proved present in the benzophenone fragment (from β-C). Thus, the Hofmann elimination of XI occurred with a mechanistically insignificant amount of phenyl migration.

In view of the readiness with which the 1,2,2-triphenylethyl carbonium ion undergoes phenyl redistribution,[16–23] we feel that the above radiochemical results definitely rule out an E1 (and probably also a "strongly E1-like") mechanism for the present elimination, whether involving classical or nonclassical cationic intermediates. The result was somewhat surprising to us, both in view of the above discussed factors which should favor carbonium ion formation, and because, with the exception of two Raney nickel catalyzed heterogeneous hydrogenolyses,[21] such complete lack of phenyl migration has never before been observed in reactions of compounds in the 1,2,2-triphenylethyl system. The results also preclude any sort of mechanism involving anchimeric assistance with concomittant migration of the phenyl groups at β-C of XI. Consistent with the radiochemical results, however, are either a fully concerted E2 mechanism, or an E1cb carbanion mechanism. The present radiochemical data do not permit a distinction between these two alternatives, and experiments designed to facilitate this distinction are currently in progress.

Experimental Section

1,2,2-Triphenylethylamine-1-C^{14} (XVIII).—Crude phenylbenzhydryl ketone-carbonyl-C^{14} (m.p. 129–131.5°) was prepared by the procedure of Bonner and Collins.[16] A portion of this product (7 g.) was diluted with nonradioactive ketone (5 g.), affording a sample having a radioactivity level of approximately 0.7 mc./mole. The material was added to a stirred mixture of reagent grade 99% formamide (36 ml.), 90% formic acid (22 ml.), and magnesium chloride hexahydrate (3 g.). The reaction vessel was fitted with a distillation assembly, and the mixture was heated to 168°, whereupon distillation of water commenced. Distillation was continued for 50 min., during which the vapor temperature arose to 105°, the temperature of the reaction mixture reached 184°, and approximately 12 ml. of water–formic acid azeotrope was collected. The heterogeneous mixture was then stirred under reflux in a nitrogen atmosphere for a period of 7 hr., whereupon an additional portion (30 ml.) of 99% formamide was added and the mixture was refluxed for another 5 hr. The reaction mixture was then cooled and treated with ice (250 cc.), after which the insoluble N-formyl derivative XVII was collected by filtration and washed with cold water. Without further purification, the solid was stirred with 7.5 *N* methanolic sodium hydroxide solution (200 ml.) and heated under reflux for 17 hr., whereupon the mixture was diluted with cold water (200 ml.) and continuously extracted with ether for a period of 7 hr. in a liquid–liquid extractor. The extracts were dried at 0° over anhydrous magnesium sulfate, decolorized by filtration through Norit, and stripped of solvent. There resulted 11.4 g. (94.7%) of crude 1,2,2-triphenylethylamine-1-C^{14}. The infrared spectrum of the oil was identical with that of an authentic sample of the amine, prepared by the sodium–ethanol reduction of phenyl benzhydryl ketoxime.[20]

Trimethyl-1,2,2-triphenylethylammonium-1-C^{14} Iodide (XIX).—A solution of the above radioactive 1,2,2-triphenylethylamine (5.5 g., 0.020 mole) in absolute methanol (25 ml.) was mixed with an excess of methyl iodide (10 ml., 0.16 mole) and 10% aqueous sodium carbonate solution (40 ml.). The reactants were sealed into an air-tight stainless steel bomb equipped with a pressure-release valve, then were heated for 8 hr. at 105°, 16 hr. at 110°, and 24 hr. at 120°. The bomb was cooled, the internal gas pressure was released, and the product was collected by filtration and dried under reduced pressure (5 mm.) over P_2O_5. The crude quaternary iodide, 7.38 g. (82.7%), m.p. 221–222° (preliminary softening), was purified by successive recrystallization from absolute methanol, affording colorless needles, m.p. 230–231°. The sample was analyzed and utilized immediately, since it appeared to deteriorate on standing.

Anal. Calcd. for $C_{23}H_{26}IN$: C, 62.30; H, 5.91; I, 28.63; N, 3.16. Found: C, 61.82; H, 6.05; I, 28.74; N, 3.16.

Trimethyl-1,2,2-triphenylethylammonium-1-C^{14} Hydroxide (XI).—An ion-exchange column was prepared using Diamond Alkali Duolite ARA-366 resin (140 g.). The column was washed and backwashed with deionized water (sp. cond. 0.2 μmho), hot aqueous methanol (80% by volume), and again with deionized water until the eluate was neutral to litmus paper. A solution of the above radioactive quaternary iodide (7.38 g., 0.0166 mole) in aqueous methanol (1.7 l., 40% MeOH by volume) was percolated through the ion-exchange column at a very slow rate. Shortly after percolation was begun, the eluate proved alkaline and showed a positive test for a quaternary ammonium compound using ammonium thiocyanate–cobaltous nitrate reagent.[25]

After all the iodide solution had passed through, the column was rinsed with 40% aqueous methanol until the eluate was no longer alkaline, the rinsings were combined with the original eluate, and the bulk of the solvent was removed by rotary vacuum evaporation at 40°. The solution was concentrated to approximately 300 ml. and reserved for the Hofmann degradation, which was conducted without isolating the solid quaternary hydroxide XI.

Hofmann Elimination of Trimethyl-1,2,2-triphenylethylammonium-1-C^{14} Hydroxide.—The above aqueous solution of XI (300 ml.) was placed in a distillation flask and heated in an oil bath. The distillation assembly terminated in a trap filled with aqueous sulfuric acid to capture the liberated trimethylamine. Distillation commenced at a bath temperature of 136° and continued for 70 min., during which the bath temperature rose to 194°. The residue was pyrolyzed at 194° for another 3 hr., whereupon the distillation assembly was cooled and rinsed with dilute hydrochloric acid and ether, collecting the rinsings in the distillation flask. The flask contents were dissolved by shaking and the two phases were separated. The aqueous phase was made strongly alkaline and extracted with ether. The latter extracts afforded no organic material on evaporation. The original ether layer was dried over anhydrous magnesium sulfate, clarified by filtration through Norit, and evaporated yielding crude triphenylethylene-C^{14} as a viscous amber oil which solidified on standing. The average yield of crude product (based on the quaternary iodide XIX) was 78% in two runs. The product was purified by chromatographing on a neutral alumina

TABLE I

SUMMARY OF RADIOCHEMICAL DATA

Compound	Spec. activity, mc./mole
Trimethyl-1,2,2-triphenylethylammonium-1-C^{14} iodide[a]	0.737 ± 0.015
Triphenylethylene-C^{14}	0.711 ± 0.000
Benzoic acid	0.722 ± 0.005
Benzophenone 2,4-dinitrophenylhydrazone	0.0025 ± 0.0002

[a] The sample was hygroscopic and absorbed water during weighing. The moisture weight, which was estimated after timing the weighings with a stop watch, was subtracted from the total sample weight in these assays.

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(25) A. M. Schwartz, J. W. Perry, and J. Berch, Jr., "Surface Active Agents and Detergents," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1958, p. 336.

column (100 g., activity II), using freshly distilled hexane as eluent. The triphenylethylene-C^{14} was finally purified by recrystallization from absolute methanol, m.p. 66.5–67.5° in agreement with the literature.[26]

Oxidative Degradation of Triphenylethylene-C^{14}.—The above triphenylethylene-C^{14} was oxidized to benzoic acid in benzophenone using potassium permanganate dissolved in aqueous acetone, adapting the procedure of Bonner and Collins.[16-20] Yields of the oxidation products were quantitative. The benzoic acid was purified by recrystallization from water, followed by sublimation, m.p. 122.4–123.2°. The benzophenone product was converted in the usual way into its 2,4-dinitrophenylhydrazone, which was purified by successive recrystallizations from ethyl acetate, m.p. 240.6–241.6°. Duplicate radioactivity assays of these products and their precursors were performed in the usual way[27,28] by wet combustion followed by counting with the aid of a Cary Model 31 vibrating-reed electrometer. The radioactivity data are summarized in Table I.

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[26] H. Adkins and W. Zartman, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 606.

[27] O. K. Neville, *J. Am. Chem. Soc.*, **70**, 3501 (1948).

[28] V. A. Raaen and G. A. Ropp, *Anal. Chem.*, **25**, 174 (1953).

Reactions of Molybdenum Pentachloride and Vanadium Tetrachloride with Alkyl- and Halobenzenes[1]

Peter Kovacic and Richard M. Lange[2]

Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106

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Isomer distributions were determined for the chlorination of toluene and halobenzenes by molybdenum pentachloride and vanadium tetrachloride. Polymeric material was the principal product from the toluene–molybdenum pentachloride reaction. With mesitylene, these metal halides yielded a mixture of bimesityl and chloromesitylene. Halogenation proceeded smoothly on treatment of benzene with vanadium tetrachloride or antimony pentachloride. The theoretical aspects are discussed.

Certain metal halides are known to effect direct halogenation of aromatic compounds.[3] Antimony pentachloride, ferric chloride, and cupric halides have received the most attention. Depending upon the metal halide, aromatic reactant, and reaction conditions other types of transformations may occur, such as nuclear coupling, side-chain attack in alkylbenzenes, and disproportionation.

The objective of the present study was to investigate the behavior of molybdenum pentachloride and vanadium tetrachloride toward simple aromatic compounds. In addition to ascertaining the nature of the products formed, we were particularly interested in orientation effects, mechanistic aspects, and comparisons with other metal halides. Although the chlorinating action of molybdenum pentachloride was noted many years ago,[4] there appears to be no specific data relative to the aromatic series. With the exception of this early cursory observation and recent reports from our laboratory dealing with molybdenum pentachloride,[5,6] there is no highly pertinent, prior literature concerning these two salts.

Results and Discussion

Most of our attention was devoted to halobenzenes (fluoro-, chloro-, and bromobenzene) and alkylbenzenes (toluene and mesitylene). In addition, studies were carried out with benzene, and with antimony pentachloride–benzene. Yields are based on the metal halide according to the pertinent stoichiometry.

Benzene.—Molybdenum pentachloride[5] and ferric chloride[7] convert benzene to *p*-polyphenyl[8] under mild conditions. The system aluminum chloride–cupric chloride is a particularly effective one for the oxidative cationic polymerization of benzene.[9,10] In all of these cases, only minor amounts of nuclear chlorination were observed.

On the other hand, halogenation was the favored route with vanadium tetrachloride which produced chlorobenzene in 66% yield. Only a negligible amount of nuclear coupling, leading to 4,4′-dichlorobiphenyl, took place. Since water functions as a cocatalyst in the polymerization of benzene by ferric chloride,[11] the influence of this Brønsted acid was investigated. At a 2:1 ratio of VCl_4:water, the yield of chlorobenzene, still the predominant product, was decreased. In addition, a small amount of solid was obtained whose infrared spectrum was very similar to that of *p*-polyphenyl. It is known that vanadium tetrachloride is rapidly converted to the oxychloride on exposure to water.[12a] A possible stoichiometric relationship for the chlorination reaction is indicated. However,

$$2VCl_4 + C_6H_6 \longrightarrow C_6H_5Cl + 2VCl_3 + HCl \qquad (1)$$

there is no direct evidence for the terminal stage of the vanadium reduction.

The antimony pentachloride–benzene reaction proceeded very smoothly with formation of chlorobenzene in 74% yield. Nuclear halogenation accounts for essentially all of the metal halide consumed. Unless conditions are carefully controlled, polychlorination occurs quite readily.[13]

$$SbCl_5 + ArH \longrightarrow ArCl + SbCl_3 + HCl \qquad (2)$$

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