prepared according to reported procedures.[3] A 0.6 M solution of the reagents in dry THF was prepared immediately prior to the reduction experiments. The organic compounds for reduction studies were obtained from Aldrich as were authentic samples of expected final products.

All reaction products were analyzed on a Hewlett-Packard 5830A GC instrument equipped with a HP18850A integrator/plotter and 5% Carbowax OV-101 (25 ft × 0.32 mm) column. The IR spectra were recorded on a Perkin-Elmer 1750 FT spectrometer. The ^{11}B NMR spectra were obtained on a JEOL FX-90Q FT NMR spectrometer operating at 28.69 MHz; shifts were measured with respect to external $BF_3 \cdot OEt_2$; ^1H NMR spectra were obtained on a Varian XL-300 spectrometer using TMS as an internal standard.

Procedure for the Reduction. The reduction of benzaldehyde in THF is representative. A 50-mL flask was fitted with a rubber syringe cap on its inlet port, a reflux condensor connected to a paraffin oil bubbler, and a magnetic stirring bar. A sample of 6 mmol (0.64 g) of benzaldehyde dissolved in 8 mL of dry THF was placed in the flask, and 2.4 mmol of reagent (4 mL, 0.6 M THF solution) was introduced via a syringe. The mixture was stirred for 30 min at room temperature and 1 h at reflux. After cooling, 0.5 mL of water was added, and the reaction mixture was stirred for 10 min, followed by addition of 0.75 mL of 30% hydrogen peroxide and refluxing for 1 h. The solution was cooled, dried over anhydrous K_2CO_3, and subjected to GC analysis.

In the reduction of 4-*tert*-butylcyclohexanone, norcamphor, and mixed benzaldehyde–acetophenone, the reagent solution was added at −10 °C, and the reaction mixture was stirred for 30 min at that temperature and then slowly brought to room temperature. The rest of the procedure corresponds to the one described above.

In the reduction of succinic anhydride and phthalic anhydride, 4.8 mmol of the reagent and 6 mmol of the anhydride were used, following the typical procedure described for benzaldehyde. After hydrolysis with hydrogen peroxide, the reaction mixture was treated with 2 mL of 6 N hydrochloric acid, gently refluxed for 1 h, cooled, dried over K_2CO_3, and analyzed on GC. In the reduction of acid chlorides to alcohols, 4.8 mmol of the reagent and 6 mmol of the acid chloride were used, following the typical procedure. In the partial reduction of acid chlorides to aldehydes, 4 mmol of the reagent was added to 12 mmol of acid chloride at −60 °C, and the temperature was maintained there for 1 h and at room temperature for 1 h, followed by hydrolysis with 2 N HCl (H_2O_2 addition was avoided to prevent oxidation of aldehyde if formed).

Reaction of $LiBH_3CRR'CN \cdot xC_4H_8O_2$ with Me_3NHCl. Trimethylamine hydrochloride (15 mmol) and $LiBH_3CRR'CN \cdot xC_4H_8O_2$ (10 mmol) were placed in a dry flask, dry THF (25 mL) was added, and the mixture was stirred under a nitrogen atmosphere at room temperature. The ^{11}B NMR spectra were taken of aliquots to monitor the progress of the reaction as time progressed (15, 30, 75, 120, and 240 min). The percentage of product formation was calculated from the chemical shift integration ratio of product to starting material. After 4 h, the reaction mixture was refluxed for 30 min, cooled, and filtered to remove LiCl and excess Me_3NHCl. The THF was removed from the filtrate on a rotary evaporator. The residue obtained was dissolved in 50 mL of CH_2Cl_2, washed with cold water (2 × 15 mL), and dried over Na_2SO_4. Upon solvent removal, the pure $Me_3N-BH_2CRR'CN$ was obtained. $Me_3N-BH_2CH_2CN$: colorless thick oil; isolated yield 91%; IR (neat) 3000 and 950 (CH), 2400 and 2372 (BH), 2221 cm^{-1} (C≡N); ^{11}B NMR ($CDCl_3$) δ 4.5 ppm (t, J_{B-H} = 99 Hz); ^1H NMR ($CDCl_3$) δ 1.4 (S, br, 2 H), 2.65 (s, 9 H).

The yields and spectral data of $Me_3N-BH_2C(Me)_2CN$ and $Me_3N-BH_2CH(Ph)CN$ correspond to the reported values.[8]

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The Reduction of (Chloromethyl)pyridines and (Chloromethyl)quinolines by Triphenyltin Hydride. The Nature of the Chlorine Atom Transfer Step[1]

Belaid Mahiou and Gerald Jay Gleicher*

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

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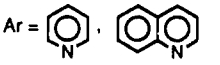
Introduction

In previous papers, we reported our findings on hydrogen atom abstraction from a series of homoaryl and heteroarylmethanes by *tert*-butoxyl[2] and undecyl[3] radicals. As part of this on going investigation on atom transfer from derivatives of methylated pyridines and quinolines, we report our results on chlorine atom transfer to triphenyltin radical. Reduction of organic halides with Group IVB hydrides is a reaction which has received intense investigation. This special attention is spurred by its growing synthetic utility[4] and suitability for mechanistic studies.[5] Gleicher and Soppe-Mbang investigated chlorine atom transfer from polycyclic homoarylmethyl chlorides[6] and related oxygen-containing heteroarylmethyl chlorides[7] to the nucleophilic[5a,8] triphenyltin radical at 70 °C. These workers utilized SCF–PPP–MO calculations to evaluate charge development in the transition state.[9] It was concluded that the rate-determining step is a direct atom abstraction and that the transition state involves an appreciable negative charge development at the benzylic carbon.[7]

It is of interest to extend this application of MO theory to the investigation of chlorine atom transfer from nitrogen containing heteroarylmethyl chlorides to triphenyltin radical (eq 1).

$$ArCH_2Cl + Ph_3Sn^{\bullet} \xrightarrow{70\ ^\circ C} ArC\dot{H}_2 + Ph_3SnCl \qquad (1)$$

Ar = 

Results and Discussion

The majority of the substrates utilized in this study were prepared by literature procedures. The relative reactivities of the heteroarylmethyl chlorides to 1-(chloromethyl)-naphthalene were determined by a direct competitive kinetic approach.[10] Using an internal standard, the relative areas of the CH_2Cl NMR signals in final reaction mixtures were compared to those found in the starting materials.

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Table I. Relative Rates of Chlorine Atoms Transfer from Homoarylmethyl and Heteroarylmethyl Chlorides to Triphenyltin Radical at 70 °C

system	k_{rel}	system	k_{rel}
benzyl chloride[a]	1.00	6-(chloromethyl) quinoline	2.11 ± 0.08
2-(chloromethyl)-naphthalene[c]	1.88 ± 0.11	8-(chloromethyl)-quinoline	2.50 ± 0.04
1-(chloromethyl)-naphthalene[c]	3.29 ± 0.38	3-(chloromethyl)-quinoline	2.92 ± 0.07
3-(chloromethyl)-pyridine	1.12 ± 0.08[b]	7-(chloromethyl)-quinoline	3.19 ± 0.04
2-(chloromethyl)-pyridine	1.38 ± 0.09	5-(chloromethyl)-quinoline	3.43 ± 0.07
4-(chloromethyl)-pyridine	1.43 ± 0.08	2-(chloromethyl)-quinoline	3.49 ± 0.33
		4-(chloromethyl)-quinoline	5.08 ± 0.08

[a] Benzyl chloride is taken as the reference compound. [b] Standard deviation. [c] Taken from ref 4.

The generally accepted mechanism for the AIBN-initiated reduction of organic chlorides by tin hydrides is shown below.

$$((CH_3)_2C(CN)-N=)_2 \xrightarrow{70\ °C} 2(CH_3)_2\dot{C}CN + N_2 \quad (2)$$

$$(CH_3)_2\dot{C}CN + Ph_3SnH \rightarrow (CH_3)_3CHCN + Ph_3Sn^{\bullet} \quad (3)$$

$$ArCH_2Cl + Ph_3Sn^{\bullet} \rightarrow ArCH_2^{\bullet} + Ph_3SnCl \quad (4)$$

$$Ar\dot{C}H_2 + Ph_3SnH \rightarrow ArCH_3 + Ph_3Sn^{\bullet} \quad (5)$$

Before the rate of disappearance of the arylmethyl chlorides can be equated to the rate of chlorine atom transfer, it is necessary to make sure that the only route for disappearance of the compounds is due to the reaction under study. Tin radicals are known to add to alkenes[5a,11] thus, the stannylation of the reactive sites in the aromatic portion of the substrate should be considered. The triphenyltin radical, however shows no apparent tendency to add to pyridine or quinoline rings. Gleicher and Soppe-Mbang[6] observed that in a direct competition between benzyl chloride and pyridine, no reaction of the latter was observed even when 95% of the benzyl chloride had reacted. A similar finding has been observed for the potentially reactive hydrocarbon, anthracene. Under our reaction conditions ring stannylation does not seem to be a problem. The other potential route for disappearance of starting material is the reaction leading to the quaternization of the ring nitrogen by arylmethyl chloride. In all the systems investigated, however, the only new NMR signals observed were those corresponding to the reduced products, 1-methylnaphthalene and heteroarylmethane. No new signals corresponding to the CH_2 attached to the ring nitrogen was observed in any of these systems.[12]

The relative rates of disappearance of the heteroarylmethyl chlorides to that of benzyl chloride are found in Table I. All systems were run in replicate. A high precision was obtained with an average standard deviation of 4% being found. Although the reactivity range between the most and the least reactive substrate investigated was only a factor of 4.5, small differences among positional isomers are apparent.

The relative reactivities obtained for the (chloromethyl)pyridines are in good agreement with those previously reported by Gleicher and Soppe-Mbang.[7] The reactivity order found is as follows: 4-P > 2-P > 3-P. This trend parallels that obtained for hydrogen atom abstraction by the nucleophilic undecyl radical.[3] It is also opposite to the trend reported by Noyce for the solvolysis of 2-pyridyl-2-chloropropanes[13] and that obtained by Taylor et al. for the pyrolysis of 1-pyridylethyl acetates.[14] These latter two reactions, which are known to involve an appreciable positive charge at the benzylic carbon in their transition states, show the 3-pyridyl isomer to be the most reactive.

The reactivity order found for the (chloromethyl)-quinolines shows the importance of conjugative stabilization in the heteroarylmethyl intermediate. The (chloromethyl)quinoline isomers having the CH_2Cl group in direct conjugation with the nitrogen atom (2-, 4-, 5-, 7-(chloromethyl)quinoline) are slightly more reactive than those having the reaction site were this conjugation is not possible.

One of the goals of the present work was to see whether the application of MO theory could allow us to conclude if the reaction under study involves a direct atom abstraction, similar to that proposed for the case of oxygen-containing heteroarylmethyl chlorides or instead some electron-transfer process. The latter possibility has been suggested for the reaction of triphenyltin radicals with polycyclic (iodomethyl)homoarenes[15] and tributyltin with substituted benzyl iodides.[8c]

In order to bring some insight into the question of nature of the rate-determining step, as well as degree of possible charge separation in chlorine atom transfer, we carried out correlations of logarithms of the relative rates with SCF[17] calculated energy differences between the arylmethyl intermediates (carbocation, carbanion, or radical) and starting materials. The starting states were taken as being equivalent to the parent, unsubstituted systems.[2,3,6,7] Although the correlation coefficients obtained were rather low, optimum correlation was found when a carbanion intermediate was used to model the transition state of the reaction under investigation. Should direct atom abstraction be operative, a polar transition state is probably involved even if a carbanion is not fully formed.

Poor results were also obtained when the logarithms of the relative rates of chlorine atom transfer were plotted against their counterparts for hydrogen atom abstraction from the corresponding homoaryl- and heteroarylmethanes by the undecyl radical.[3] The correlation coefficient obtained was 0.53.

The poor nature of the correlations should not be unexpected. Table I shows reactivities which seem related more to the nature of the aryl group than to positional factors. In the case of hydrogen atom abstraction by either the electrophilic *tert*-butoxyl[2] or nucleophilic undecyl[3] radicals, the 4-methylquinoline/4-methylpyridine and 2-methylquinoline/2-methylpyridine pairs had comparable reactivities. In the present study, however, 4-(chloromethyl)quinolene is 3.6 times more reactive than 4-(chloromethyl)pyridine. A similar situation exists of the 2-isomers. Furthermore, the seven (chloromethyl)quinoline isomers show a reactivity range of only 2.5. The corresponding methylquinolines showed a reactivity range of

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Table II. Averages of the Relative Rates of Chlorine Atom Transfer and Relative LUMO Energies of the Parent Systems

system	average k_{rel}[a]	log average k_{rel}	ΔE_{LUMO}[b]
benzene	1.00	0.00	0.00
pyridine	1.31 ± 0.17[c]	0.12 ± 0.05	−0.45
naphthalene	2.59 ± 1.00	0.41 ± 0.15	−0.86
quinoline	2.87 ± 1.47	0.46 ± 0.18	−1.18

[a] Obtained by averaging the relative rates of positional isomers. [b] SCF-PPP calculated LUMO energies in electron volts. [c] Standard deviation.

13.5 in hydrogen atom abstraction by the nucleophilic undecyl radical.[3] Hammett studies on the reaction of substituted benzyl chlorides with tributyltin radical[8b,c] and substituted toluenes with undecyl radical[17] suggest that the latter should not be the inherently more selective system. These results suggest that chlorine atom transfer from the heteroarylmethyl chlorides to triphenyltin might not involve direct atom abstraction.

The literature contains previous reports on possible electron-transfer involvement in the rate-determining step of halogen atom transfer to organotin[8c,15] and organogermanium[18] radicals. Very recently, Bordwell and Harrelson have reported that the substitution reactions of certain benzylic chlorides may take place by either electron transfer or direct displacement depending on the nature of the nucleophile.[19] If the chlorine atom transfer from homoaryl- and heteroarylmethyl chlorides to triphenyltin radical involves an electron transfer in this step, LUMO energies of the aromatic portion of our molecules might be a reasonable parameter with which to correlate the present relative reactivities.

The logarithms of the average relative rates of chlorine atom transfer for each parent system and SCF-PPP[14] LUMO energy difference between the parent unsubstituted system and benzene are listed in Table II. Although this is only a crude approximation, a correlation coefficient of 0.99 was obtained when the logarithms of the average relative reactivities were plotted against the LUMO energy differences.

Conclusion

The relative rates of triphenyltin hydride reduction of (chloromethyl)quinolines and (chloromethyl)pyridines were obtained. The poor nature of the correlations obtained with SCF–PPP calculated energies tend to support the view that the rate-determining step does not involve a direct atom abstraction as was observed in hydrogen atom transfer from the corresponding heteroarylmethanes. An electron transfer might be operative in the reduction of these nitrogen containing heteroarylmethyl chlorides. Further theoretical investigations are underway.[20]

Experimental Section

All compounds and solvents were purified by standard procedures before use.[21] Melting points were measured with a Büchi melting point apparatus. Melting points are uncorrected. Nuclear magnetic spectra were recorded on a Bruker AM-400 or AC-300 MHz instruments using tetramethylsilane as reference and deuteriochloroform or perdeuteriobenzene as solvent.

Compounds. The compounds utilized in this study were all prepared using literature procedures except 1-(chloromethyl)-naphthalene and 2- and 4-(chloromethyl)pyridine which are commercially available. The remaining isomer, 3-(chloromethyl)pyridine, was prepared from the commercially available carbinol using the procedure of Kaslow and Schlatter.[22] The majority of the (chloromethyl)quinoline isomers were prepared from the methylquinolines by one of the two methods described below. The only exception, 3-(chloromethyl)quinoline, was prepared from 3-bromoquinoline.

Table III. Selected Physical Properties of the (Chloromethyl)quinoline Isomers

isomer	mp, °C	lit. mp, °C	δ^c CH_2Cl, ppm
2	54–56	54–55.7[a]	4.82
3	33	33–34[b]	4.71
4	57	56–57[a]	5.02
5	90–90.5	88–89.5[b]	5.02
6	71	70.5–71[b]	4.15
7	54–55	53–54[b]	4.79
8	54	53.5–54.5[b]	5.39

[a] Reference 24. [b] Reference 22. [c] In $CDCl_3$ and relative to TMS.

Method A: Preparation of 2- and 4-(Chloromethyl)-quinoline. Either 2- or 4-methylquinoline was oxxidized to the *N*-oxide with aqueous hydrogen peroxide.[23] The *N*-oxide was then treated with tosyl chloride and boron trifluoride in DMF according to the method of Ochiai to yield the (chloromethyl)-quinoline.[25]

Method B: Preparation of 5-, 6-, 7-, and 8-(Chloromethyl)quinoline. The appropriate methylquinoline was oxidized to the aldehyde using selenium dioxide.[25] The aldehyde was then reduced to the (hydroxymethyl)quinoline with sodium borohydride in methanol. The carbinol was converted to the (chloromethyl)quinoline by using the procedure of Kaslow and Schlatter.[22]

Preparation of 3-(Chloromethyl)quinoline. Commercially available 3-bromoquinoline was converted to 3-quinolinecarboxylic acid using the method of Gilman and Spatz.[26] The carboxylic acid was then esterified upon treatment with diazomethane in either at 0 °C.[27] The ester was then reduced to the carbinol using sodium–bis(2-methoxyethoxy)aluminum hydride. The 3-(hydroxymethyl)quinoline was then converted to 3-(chloromethyl)quinoline by the usual method.[22]

The purity of each (chloromethyl)quinoline was determined by NMR analysis which showed nonaromatic signals for only a chloromethylene group. The chemical shifts in question, along with observed and literature values for melting points, are found in Table III.

Kinetics. Solutions of 1-(chloromethyl)naphthalene, the chosen heteroarylmethyl chloride, α,α'-azobisisobutyronitrile, internal standard (*p*-di-*tert*-butylbenzene), and perdeuterobenzene in approximate molar ratio of 10:10:1:1:600 were prepared. A small amount was reserved for analysis of starting material. To the remaining solution was added triphenyltin hydride in an approximate molar ratio of 1:2 relative to 1-(chloromethyl)-naphthalene. This final solution was equally divided into several ampoules. The ampoules were sealed under a reduced pressure of nitrogen after a series of freeze–thaw cycles. They were then put in a constant-temperature oil bath maintained at 70 ± 1 °C for 2 h. After completion of the reaction, the ampoules were cooled and opened. The reaction mixtures were analyzed for the disappearance of the chloromethylarenes via NMR using the aliphatic protons of *p*-di-*tert*-butylbenzene as an internal standard.

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Benzylic Bromination by Bromotrichloromethane. Dependence of the Identity of the Chain-Carrying Radical(s) on the Method of Initiation[1]

Kevin W. Krosley and Gerald Jay Gleicher*

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

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Introduction

The photoinitiated free-radical reactions of bromotrichloromethane date back to 1947 when Kharasch and co-workers reported its addition to a series of olefins.[2] These reactions proceed by a mechanism which involves addition of the trichloromethyl radical as the rate-determining step. Bromotrichloromethane has also been used to effect benzylic brominations.[3] As might be expected, analogous allylic bromination is complicated by the competing addition to the double bond.[4] Even in allylic systems, however, hydrogen atom abstraction, which is the rate-determining step in the bromination process, may become comparable to addition if the lability of the allylic hydrogen atom is increased or the accessibility of the double bond is decreased.[5]

The study of substituent effects in the course of benzylic brominations has led to a natural utilization of Hammett type relationships. While an earlier study by Kooyman, van Helden, and Bickel reported no dependence of rate on substituent,[6] a later study by Huyser has shown that a substantial substituent effect ($\rho = -1.46$, correlated with σ^+) is associated with the photoinitiated reaction of a series of substituted toluenes with bromotrichloromethane at 50 °C.[7] A generalized mechanism, Scheme I, has been proposed which involves the trichloromethyl radical as the chain carrying (hydrogen atom abstracting) species in this benzylic bromination. Support for this mechanism has come from gas-phase reactions of bromotrichloromethane with alkanes in which only brominated products and chloroform were observed.[8]

A second possible mechanism of photoinitiated benzylic bromination by bromotrichloromethane has been postulated on several occasions, Scheme II.[8-10] Although initially discounted as a major pathway based on observed products[8] and selectivities,[9] support for this mechanism, which involves chain propagation by the bromine atom, has been presented by Tanner and co-workers.[10,11] A repetition of Huyser's study produced similar results ($\rho = -1.24$, correlated with σ^+). It was shown, however, that when these brominations were carried out in the presence of a hydrogen bromide trap such as ethylene oxide or potassium carbonate, the sensitivity to substituents decreased markedly ($\rho = -0.69$, again correlated with σ^+). Furthermore, under normal photoinitiation conditions (no hydrogen bromide trap), substantial hydrogen/deuterium exchange is observed when mixtures of toluene and toluene-d_3 are used. This scrambling is completely suppressed upon addition of ethylene oxide. Both of these observations are consistent with the reversibility of the hydrogen abstraction step in the bromine atom propagation mechanism.

Scheme I. Mechanism Involving Hydrogen Atom Abstraction by the Trichloromethyl Radical in the Photoinitiated Benzylic Bromination of Toluenes by Bromotrichloromethane

$$BrCCl_3 \xrightarrow{h\nu} Br^\bullet + {}^\bullet CCl_3$$

$$ArCH_3 + {}^\bullet CCl_3 \rightarrow ArCH_2^\bullet + HCCl_3$$

$$ArCH_2^\bullet + BrCCl_3 \rightarrow ArCH_2Br + {}^\bullet CCl_3$$

Scheme II. Mechanism Involving Hydrogen Atom Abstraction by the Bromine Atom in the Photoinitiated Benzylic Bromination of Toluenes by Bromotrichloromethane

$$BrCCl_3 \xrightarrow{h\nu} Br^\bullet + {}^\bullet CCl_3$$

$$ArCH_3 + Br^\bullet \rightleftarrows ArCH_2^\bullet + HBr$$

$$ArCH_2^\bullet + BrCCl_3 \rightarrow ArCH_2Br + {}^\bullet CCl_3$$

$$HBr + {}^\bullet CCl_3 \rightarrow Br^\bullet + HCCl_3$$

Is hydrogen atom abstraction by bromine atom the sole chain-carrying step? Several studies on substituted alkylbenzenes have been carried out which show distinctly different selectivities for bromotrichloromethane brominations and brominations using either molecular bromine or *N*-bromosuccinimide (NBS).[12] On the basis of bond energies (enthalpies of reaction), hydrogen atom abstraction from toluene by trichloromethyl radical (10.8 kcal/mol) should be favored over that by bromine atom (2.4 kcal/mol).[14] For the Scheme II mechanism to be the only one operative also requires the trichloromethyl radical to react in an unusually selective fashion. It demands exclusive reaction with a small, steady-state concentration of hydrogen bromide even though that of the benzylic substrate is several orders of magnitude greater at any given time of the reaction.

Neither of the two mechanisms, when considered alone, is able to account for all of the observations which have been reported for these photoinitiated brominations. A possible adjudication of the question may be found through generation of the trichloromethyl radical in a less ambiguous fashion.

Results and Discussion

Initial attempts to generate the trichloromethyl radical in an unambiguous fashion were not successful. Trichloroiodomethane was deemed to be a suitable precursor

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