ELECTROPHILIC RADIOBROMINATIONS OF HIPPURIC ACID: AN EXAMPLE OF THE UTILITY OF ARYLTRIMETHYLSILANE INTERMEDIATES*

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SUMMARY

An investigation of the use of an aryltrimethylsilane intermediate to obtain p-[^{77}Br]bromohippuric acid (12) was carried out. The silane intermediate, p-trimethylsilylhippuric acid (11), was radiobrominated with carrier-added and no-carrier-added levels of bromine-77 to give isolated yields of 73% and 49% of 12 (respectively). Initial radiobromination studies were carried out with p-trimethylsilylbenzoic acid (1) to evaluate the feasability of the approach. Radiobrominations of 1 yielded 70-93% radiolabeling efficiencies. All of the radiobrominations could be accomplished within 15 minutes, indicating that the method could be applicable to use of the shorter lived radionuclides of bromine.

Key Words: Hippuric Acid, Radiobromination, Bromine-77, p-Trimethylsilylhippuric Acid, p-Trimethylsilylbenzoic Acid

INTRODUCTION

Radioiodine labeled hippuric acid has been used extensively for the evaluation of renal function in man. This has been possible due to the fact that hippuric acid and its aromatic ring substituted derivatives are efficiently cleared from the blood by the kidneys.[1] While radioiodine labeled hippuric acid, particularly iodine-123 labeled, will continue to be clinically useful, other radiolabels for hippuric acid such as the radionuclides of bromine, should be investigated. Indeed, the increased stability of the aryl-bromine bond;[2] the fact that radiobromine does not accumulate in the thyroid;[3] and the possible use of positron-emitting radionuclides of bromine (e.g., bromine-75), makes radiobromine an attractive alternative for radioiodine.

Prior to the biological evaluation of radiobromine labeled hippuric acid, a method of radiobrominating hippuric acid which is rapid and efficient needs to be made available. Van Wyke et.al.[4] have described the synthesis of bromine-77

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($T_{1/2}$=57 h,γ=239 and 521 keV) labeled o-hippuric acid, but the exchange reaction is slow and the radiochemical yields were low. Another method of radiobrominating hippuric acid has been described by Ache et.al.[5,6] where they use a "gas exposure" technique. Their technique, which is most likely an electrophilic radiobromination, has the drawback that it involves the handling of a radioactive gas, and its application has not been demonstrated with radionuclides other than bromine-80m ($T_{1/2}$=4.4 h,γ=37 keV).

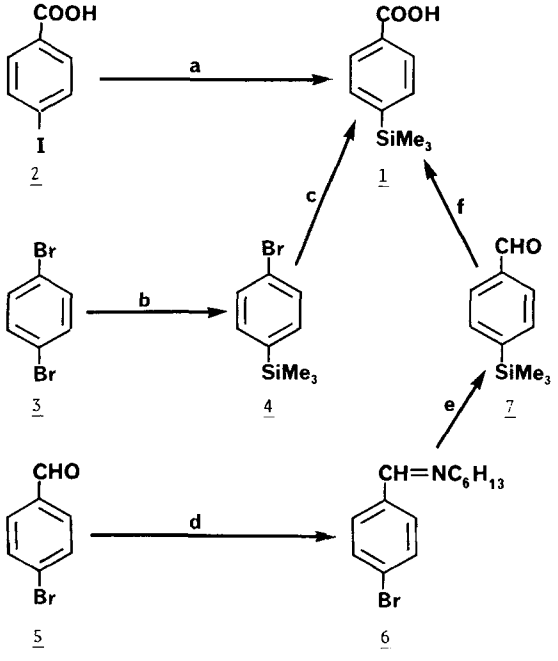
Our previous studies of incorporating radiobromine into aromatic rings via aryltrimethylsilane intermediates[7,8] led us to investigate the application of such an intermediate for radiobrominations of hippuric acid. Since the radiobrominations of deactivated aromatic rings that contained a trimethylsilyl group had not previously been studied,[9] an investigation of the brominations of p-trimethylsilylbenzoic acid (1) was carried out initially. As these radiobrominations were successful, p-trimethylsilylhippuric acid (11) was synthesized, and the radiobrominations of this compound were studied. The syntheses of 1 and 11 and the subsequent radiobrominations of these compounds are described here.

RESULTS AND DISCUSSIONS

While any of the three isomeric trimethylsilylhippuric acids might have been studied, we chose to study the radiobrominations of the para substituted compound because radiobrominations at the para position would be the most difficult to accomplish by other methods, and the product should be quite stable. Even though most of the radioiodinations of hippuric acid have been directed at labeling in the ortho position, the only apparent reason for labeling in the ortho position is that the radioiodine exchange reactions are more facile than in the meta or para positions.[10] Furthermore, studies of meta-labeled hippuric acid[11] have shown that there is essentially no difference in renal clearance between the ortho and meta ring substituted compounds, except for the stability of the radiolabel.[12] Evaluation of these data along with the "three point attachment" model put forth by Moller and Sheikh in their review,[1] reinforced our choice of the para position for radiolabeling.

Initial radiobromination studies were carried out using p-trimethylsilylbenzoic acid (1). Synthesis of 1 was accomplished via three different routes (Scheme I). Direct lithiation/silylation of p-iodobenzoic acid (2)[13] at -78°C yielded a mixture of products, of which only approximately 30% was the desired product. Difficulty in purification of 1 from the mixture led to investigation of other methods to synthesize 1. A second synthetic pathway which involved two consecutive Grignard reactions on p-dibromobenzene (3) was also tried. Unfortunately, while the silylation of 3 to yield 4 could be accomplished in high yields,[14] the subsequent carboxylation[15] gave poor results.[16] A third synthetic route was developed which had more steps, but was easily carried out to give good overall yields of 1 (58% of theory from 5). In that synthesis, p-bromobenzaldehyde (5) was reacted at 135°C with cyclohexylamine[17] to give 6. The

SCHEME I: Syntheses of p-Trimethylsilylbenzoic Acid



a)n-BuLi/TMSCl b)Mg/TMSCl c)Mg/CO_2 d)$C_6H_{13}NH_2$/Δ
e)n-BuLi/TMSCl;H_3O^+ f)Ag_2O

silylation of 6 was followed by acid workup to yield p-trimethylsilylbenzaldehyde (7). The subsequent conversion of 7 to 1 was accomplished by Ag_2O oxidation[18] or air oxidation.[19]

The radiobrominations of 1 using $Na^{77}Br$ with added carrier NaBr (ca) were studied in MeOH and HOAc. Reactions using N-chlorosuccinimide (NCS) as an oxidant gave poor yields of the desired radiobrominated product, 8. However, when tert-butylhypochlorite (TBHC) was used as the oxidant, 90-93% radiochemical yields were obtained within 10 minutes when the reaction was run at room temperature in HOAc, and within 10 minutes when the reaction was run at 50°C in MeOH. The only difference observed between the radiobrominations in MeOH or HOAc was that the reactions were slower in MeOH.

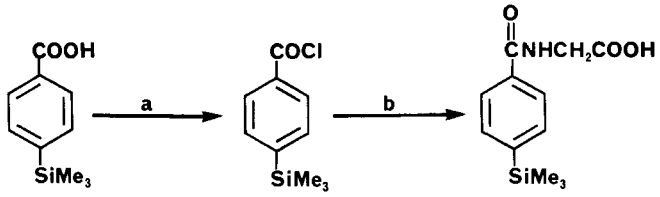
1 8

The no-carrier-added (nca) radiobrominations of 1 were found to be more difficult to accomplish. Reactions employing identical conditions to those that gave only one product in the ca radiobrominations, gave mixtures of radiobrominated products when nca radiobromine was used. Interestingly, the nca radiobromination reactions in which crude samples of 1 were used gave different radiobrominated products depending on the method by which 1 was synthesized, even though the HPLC analyses of the samples showed no difference in purity (all were >99% pure). For example, 1 produced by air oxidation of 7 gave a large mixture of radiobrominated products, whereas reaction of 1 produced by Ag_2O oxidation of 7 gave three major radiobrominated products. The nca radiobromination reactions of purified 1 using TBHC in MeOH gave a very lipophilic radiobrominated product which was not identified. However, the nca radiobromination

reactions of purified 1 using TBHC in HOAc at 50°C gave 8 in radiochemical yields of 70-81% within 15 minutes.

Synthesis of the requisite p-trimethylsilylhippuric acid was accomplished (Scheme II) by the preparation of the acid chloride 10,[20] followed by reaction of 10 with glycine in aqueous NaOH.[21] The reaction gave a mixture of approximately 80% of 11 and 20% of 1. Fortunately, due to the difference in solubility of these compounds in acetonitrile, it was relatively easy to obtain 11 very pure.

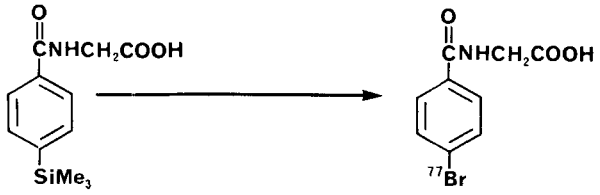
SCHEME II: Synthesis of p-Trimethylsilylhippuric Acid



1 10 11

a) $SOCl_2$ b) $H_2NCH_2CO_2H/NaOH$

The ca radiobrominations of 11 were carried out under the same reaction conditions as used for the ca radiobrominations of 1. Thus, reaction of 11 in MeOH (or HOAc) solution of $Na^{77}Br$ containing added NaBr with TBHC gave only one product by radioHPLC. The radioactivity peak had a retention time identical to that of p-bromohippuric acid and contained 93% of the observed radioactivity. A preparative scale ca radiobromination of 11 started with 4 mCi of $Na^{77}Br$ gave 12 in an isolated yield which contained 92% of the radioactivity that was injected into the HPLC or 73% (2.9 mCi) of the initial activity. The radiochemical yield was not optimized as only part of the reaction mixture was taken out of the reaction vial; optimized yields of 73-92% might be obtained for this reaction.



11 12

Unlike the nca radiobrominations of 1, the nca radiobrominations of 11 were accomplished using the same reaction conditions as were used for the ca radiobrominations. In fact, the nca radiochromatograms were almost identical to those obtained with the ca radiobrominations, having about 93% of the activity observed being associated with the peak corresponding to 12. However, in a preparative scale reaction using 4 mCi $Na^{77}Br$ only 76% of the radioactivity that was injected into the HPLC was isolated as 12, and this was only 49% (1.95 mCi) of the initial activity. As in the ca reaction, no optimization of the radiochemical yield was made. The smaller isolated yields appear to be due to appreciable quantites of radioactivity remaining in the syringe, HPLC injection port, and on the column. Optimized radiochemical yields might therefore be between 49% and 76%.

Considering the problems encountered in the radioiodinations of o-iodohippuric acid which contained small quantities of o-iodobenzoic acid,[22] it was of interest to look at the product composition when 11 was allowed to react in the presence of 1. Reaction of a mixture of equal quantities of 1 and 11 (by weight) with ca $Na^{77}Br$/TBHC gave a nearly 1:1 mixture of 8 and 12. Since this result indicates that there is not a large difference in the radiobromination reactions of 1 and 11, trace impurities of 1 that might remain after purification of 11 should not be a problem in the radiobrominations.

CONCLUSIONS

The use of an aryltrimethylsilane intermediate to introduce bromine-77 into the para position of hippuric acid has been demonstrated. The ipso electro-

philic substitution reactions were found to be rapid, giving high radiochemical yields within 15 minutes. The fact that the substitution reaction is so facile suggests that this method might also be used to introduce other radionuclides of bromine into hippuric acid. Incorporation of the radiobromine into the para position of the aromatic ring has yielded a very stable product as no decomposition of the labeled compound was observed after 24 hours at room temperature.

While the synthesis of the trimethylsilylhippuric acid is necessary, the synthesis can be readily accomplished by the route described here. As only milligram quantities are used for each reaction, sufficient amounts of the compound can be made at one time for a very large number of reactions. No decomposition of 11 has been observed after being stored at room temperature for approximately 6 months.

EXPERIMENTAL

General

The reagents, solvents, and aromatic compounds 2, 3, and 5 were purchased from commercial sources as analytical reagent grade and were used as obtained. Tetrahydrofuran used as the solvent in metal-halogen exchange reactions was distilled from sodium/benzophenone. The tert-butylhypochlorite was prepared by a literature procedure.[23] The bromine-77 was produced by proton irradiation of a molybdenum target as previously described.[24] Purification of the $Na^{77}Br$ samples was accomplished by ion chromatography, and samples were obtained as $Na_2CO_3/NaHCO_3$ solutions.

Proton NMR spectra were obtained on a Varian EM-360A (60 MHz) instrument, and the chemical shifts are reported as ppm from TMS. IR spectra were obtained on a Perkin-Elmer model 283 spectrophotometer. Elemental analyses were obtained from Galbraith Laboratories (Knoxville, Tenn.). Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Analyses of the radiobromination reactions were carried out by HPLC using both UV (280 nm) and radioactivity detectors. The HPLC system consisted of two Waters 6000A pumps, a Waters U6K injector, a Kratos 773 UV spectrophotometer, and a Waters Data Module and System Controller. The radioactivity detector consisted of a 2-inch NaI crystal, Ortec power bin, high-voltage supply, rateme-ter, amplifier, counter/timer, and line printer. Separations were accomplished using a Waters Radial Compression Module with a Radial-Pak C-18 cartridge. The eluting solvent mixture (by volume) was 60% MeOH and 40% of a 1% HOAc (in H_2O) solution. Radiobromide eluted with the solvent front. Retention times for p-bromobenzoic acid and p-trimethylsilylbenzoic acid were 6.5 minutes and 18.6 minutes respectively at a flow rate of 2 mL/min. Retention times for p-bromo-hippuric acid and p-trimethylsilylhippuric acid were 2.9 minutes and 8.6 minutes respectively at a flow rate of 1 mL/min. Some differences in the retention times were noted depending on the solvent used in the reaction and volume put into the HPLC, but retention times could be confirmed by similar conditions with standards. Radioactivity in the reactions was assayed by using a Capintec Radioisotope Calibrator (CRC-10). Reaction vessels and collection vials (for HPLC) were placed in the ionization chamber in a plastic sample holder. Syr-inges containing activity were counted by using an adaptor in the sample holder. No corrections for the variations in the geometry of the radioactive samples were made.

Synthesis of p-Bromobenzocylcohexylimine (6).

A mixture of 30.0g (0.162 mol) p-bromobenzaldehyde and 21 mL (18.0g - 0.18 mol) cyclohexylamine was heated to 135°C for 1 h under a stream of argon. The reaction solution was allowed to cool to room temperature whereupon it solidi-fied, yielding 41.6g of a crude light yellow solid. The crude material was dissolved in 150 mL of hot CH_3CN and then cooled in an ice/H_2O bath. The color-less flakes were collected and dried to yield 26.7g (61.4%) of 6, mp 61.5-63.5°C. An additional 9.04g (20.8%) of 6 was collected by reducing the volume of CH_3CN and cooling in an ice/H_2O bath.

An analytical sample of 6 was obtained by recrystallization from CH_3CN, mp 62-64°C. NMR($CDCl_3$,δ) 8.31(s,1H), 7.62(s,4H), 3.23(m,1H), 2.2-1.0(m,12H); IR(Nujol, cm^{-1})1643, 1068, 819.

Synthesis of p-Trimethylsilylbenzaldehyde (7).

A solution of 30.0g (0.112 mole) of 6 in 300 mL anhydrous THF was cooled to -78°C under argon and 75 mL of a 1.6M n-BuLi/hexane solution (0.120 mol) was added dropwise over 20 minutes. To the resultant thick brown solution was added 50 mL (0.40 mol) trimethylsilyl chloride (TMSCl) in 5 min. The reaction mixture was stirred at -78°C for 30 min, then the Dry Ice/acetone bath was removed. The reaction mixture was allowed to stir overnight at room temperature. To the resulting colorless solution was added 300 mL of a saturated $(NH_4)_2CO_3$ solution (slowly at first). The two phases were separated; and a saturated solution of NH_4Cl in 1M HCl was added. The solution was shaken well and the two layers were separated. The organic phase was washed with saturated NH_4Cl, dried over $MgSO_4$, and evaporated to give 26.4g of a residue. The residue was triturated with hexanes and filtered. The filtrate was evaporated to an oil. The oil was purified by Kugelrohr distillation at 50°C/0.01 torr to yield 15.9g (79.8%) of 7 as a colorless oil. (bp reported[19] 118°C/15 torr) NMR($CDCl_3$,δ) 10.10(s,1H), 7.80(d,2H,J=8Hz), 7.79(d,2H,J=8Hz), 0.29(s,9H). IR(neat,cm^{-1}) 1702, 1600, 865-820 (b).

Synthesis of p-Trimethylsilylbenzoic Acid (1).

a) To a solution of 1.05g (5.9 mmol) of 7 dissolved in 20 mL of 5% NaOH and 20 mL MeOH was added 1.42g (6.1 mmol) Ag_2O portionwise. After the addition was complete, the reaction solution was stirred for 30 minutes at room temperature. The reaction solution was filtered through Celite, and the solids were washed with 25 mL of a 10% NaOH solution. The filtrate was cooled in an ice/H_2O bath and was acidified with conc. HCl. The resultant white solid was collected and washed well with H_2O. The solid was then dissolved in ether; the ether was

dried over $MgSO_4$ and evaporated to yield 1.01g (88.3%) of a white solid, mp 114-116°C.

An analytical sample was prepared by recrystallization from hexane to yield colorless plates, mp 116.5-117.5°C (reported[20] 117-118°C). NMR($CDCl_3$,δ) 8.71 (bs,1H), 8.13 (d,2H,J=8Hz), 7.67(d,2H,J=8Hz), 0.31(s,9H). IR(nujol, cm^{-1}) 1691, 1390, 1190, 832.

b) A stream of air was passed over 5.0g (28 mmol) of 7 in a 50 mL flask for 3 days at room temperature. During that time the oil changed to a colorless solid. The solid was dissolved in 15% KOH, and this solution was extracted with ether. The KOH solution was acidified with conc. HCl. The white precipitate was collected and dried under vacuum to yield 3.25g (59.6%) of 1, mp 114.5-116.5°C. The ether layer was washed with H_2O, dried over $MgSO_4$, and evaporated to yield 0.55g (11%) of the starting aldehyde, 7. An analytical sample was prepared as above, mp 116.5-117.5°C.

Synthesis of p-Trimethylsilylhippuric Acid (11).

A solution of 2.0g (10.3 mmol) of 1 in 10 mL thionyl chloride was heated to reflux for 1.5 h. The excess thionyl chloride was removed by distillation at a low vacuum. The residue was purified by Kugelrohr distillation at 70°C/0.01 torr to yield 1.84g (84%) of 10 as a colorless oil. The acid chloride was then added dropwise to a solution of 1.0g glycine in 10 mL NaOH at room temperature. The reaction mixture turned a light yellow color and became thick immediately. The thick solution was stirred for an additional 10 minutes and was poured onto ice. Concentrated HCl was added until the suspension became acidic. The thick suspension was diluted with H_2O and filtered. The filtered solid was rinsed well with H_2O and dissolved in ether. The ether was dried over $MgSO_4$ and evaporated under vacuum to yield 1.87g of a white solid, mp 151-165°C. HPLC and NMR analyses indicated that the solid contained approximately 20% of 1 and 80% of 11. Recrystallization of the crude product from 50 mL of hot CH_3CN yielded 1.00g (46% based on 10) of 11, mp 190.5-192°C. An additional 0.13g (6%) of 11

was obtained by cooling the filtrate in an ice/H_2O bath. The CH_3CH was evaporated to yield 0.70g of a yellow solid which was a mixture of 1 and 11. No further separation of the two products was attempted.

An analytical sample of 11 was obtained by recrystallization from CH_3CN, mp 190.5-191.5°C. NMR($CDCl_3$,δ) 8.13(bs,1H), 7.96(d,2H,J=8Hz), 7.67(d,2H,J=8Hz), 4.13(m,2H), 0.28(s,9H). IR(nujol,cm^{-1}) 3250, 1791, 1218, 835. Elemental Analysis: Calc. C; 57.34, H; 6.82 Found C; 57.53, H; 6.64.

Radiobrominations of 1; Synthesis of 8.

Carrier-Added: To a vial containing 100 µL of a 1 mg/mL solution of NaBr in HOAc (or MeOH) was added 2 µL of a $Na^{77}Br$ solution (512 µCi). To this solution was added 1 µL TBHC, followed by 2 mg of 1. Reaction progress was followed by radioHPLC. After 10 minutes at room temperature, the reaction carried out in HOAc had 93% of the radioactivity observed in the radiochromatogram in the peak corresponding to 8. The same reaction conditions using MeOH as the solvent had only 51% of 8 in 15 minutes, however in another reaction, elevation of the reaction temperature to 50°C resulted in 88% of the radioactivity being contained in the peak corresponding to 8 within 20 minutes.

No-Carrier-Added: A 5 µL aliquot of a $Na^{77}Br$ solution (500 µCi) was evaporated to dryness under vacuum at 70°C. To the cooled vial was added 100 µL HOAc and 2 mg of recrystallized 1. To this solution was added 1 µL of freshly prepared TBHC. The reaction vessel was then placed in a heating block at 50°C. The reaction progress was followed by radioHPLC and was found to be complete within 10 minutes. The amount of radioactivity present as 8 varied from 70-81% in several different runs.

Radiobrominations of 11; Synthesis of 12.

Carrier-Added: To a vial containing 5 µL (4.01 mCi) of a $Na^{77}Br$ solution was added 50 µL of a 1 mg/mL solution of NaBr (50 µg, 0.049 µmol) in MeOH. To this solution was added 1 µL TBHC (0.9 mg, 8.3 µmol) followed by 2.0 mg (8.0 µmol) of 11. The reaction vessel was then placed in a heating block at 50°C for

15 minutes. After 15 minutes, most of the reaction solution was withdrawn into a syringe (3.30 mCi) and was injected into the HPLC. Some radioactivity remained in the syringe (0.14 mCi) so the total activity that was injected into the HPLC was 3.16 mCi. Isolation of the p-[^{77}Br]bromohippuric acid peak yielded 2.92 mCi of 12. The isolated activity represented 93% of the activity put in the HPLC or 73% of the initial activity. The isolated product was checked by HPLC and found to be >99% radiochemically pure. No decomposition was seen in this product after 24 hours at room temperature.

No-Carrier-Added: To a vial containing 5 μL (4.00 mCi) of a Na^{77}Br and 50 μL of HPLC grade MeOH was added 1 μL of freshly prepared TBHC. Quickly thereafter, 2 mg of 11 was added to the solution. The vial was placed in a heating block at 50°C for 20 min, and most of the reaction solution was taken up in a syringe (2.93 mCi). Of the activity in the syringe 2.56 mCi was injected into the HPLC, and 1.95 mCi was isolated as 12. The isolated yield represented 76% of the radioactivity put into the HPLC and 49% of the initial activity. Monitoring of the HPLC showed that a large amount of radioactivity remained on the column and in the injection port of the HPLC.

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