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SYNTHESIS OF ^{13}C-LABELED POLYCHLORINATED BIPHENYLS

Robert W. Roth*, J. Richard Heys**, Joseph H. Saugier*,
David H. T. Chien*, Gary A. Rotert*, and Mitchell D. Erickson

Midwest Research Institute, 425 Volker Boulevard
Kansas City, Missouri 64110, U.S.A.

SUMMARY

Methods are described for the synthesis of 4-chloro(1',2',3',4',5',6'-$^{13}C_6$)biphenyl; 3,3',4,4'-tetrachloro($^{13}C_{12}$)biphenyl; and 2,2',3,3',5,5',6,6'-octachloro($^{13}C_{12}$)biphenyl; decachloro($^{13}C_{12}$)biphenyl from ($^{13}C_6$)benzene of $\geq$ 99 atom % isotopic purity, on scales of 100 mg to 1 g. The gas chromatographic retention time of each ^{13}C-polychlorinated biphenyl (PCB) matched that of the corresponding unlabeled commercial reference standard, and the mass spectrum of each compound was consistent with an isotopic purity of $\geq$ 99 atom % ^{13}C. These compounds are useful as recovery surrogates and internal standards in the determination of PCBs in a variety of complex matrices.

Key Words: 4-Chloro(1',2',3',4',5',6'-$^{13}C_6$)biphenyl; 3,3',4,4'-Tetrachloro-($^{13}C_{12}$)biphenyl; 2,2',3,3',5,5',6,6'-Octachloro($^{13}C_{12}$)biphenyl; Decachloro($^{13}C_{12}$)biphenyl

INTRODUCTION

In connection with a program to develop analytical methodology for the determination of polychlorinated biphenyls (PCBs) in a variety of environmental and industrial matrices (1-5), we were interested in the synthesis of several specific PCB congeners labeled with ^{13}C. These compounds were to be used as recovery surrogates or internal standards for use in gas chromatographic/electron impact mass spectrometry (GC/EIMS) methods. These methods would be applicable

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* Current address: Chemsyn Science Laboratories, 13605 West 96th Terrace, Lenexa, Kansas 66215-1297.

** Current address: Smith, Kline and French Laboratories, 1500 Spring Garden Street, Philadelphia, Pennsylvania 19101.

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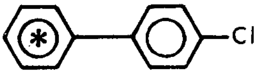
for any or all PCB congeners and isomers of natural isotopic abundance which might be encountered in analytical samples. The particular four compounds synthesized were chosen because of the need to provide surrogates representing the entire range of PCB congeners (i.e., Cl_1 to Cl_{10}) and because of the efficiency of synthetic methods available or readily developed. Gram quantities of all four compounds were desired, and high purities were required in order to avoid contamination of samples resulting from spiking with the labeled standard.

Calculations of mass spectral molecular ion series for various labeled PCB congeners, assuming different numbers of chlorine substituents and either six or twelve carbons enriched with ^{13}C to various extents, revealed that for PCBs possessing three or fewer chlorines, enrichment of only one ring (to 99 atom % ^{13}C) was sufficient to provide complete separation of labeled and natural abundance species in the mass spectrum. PCB surrogates with four or more chlorine atoms, however, needed to be enriched with ^{13}C at all positions. In all cases, enrichment with ^{13}C was preferable to ^{37}Cl in terms of either mass spectral resolution from the natural abundance analog or cost or difficulty of synthesis.

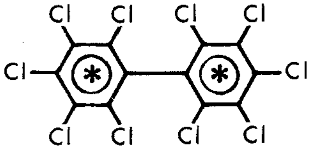
RESULTS AND DISCUSSION

A wealth of information is available on the synthesis of PCBs (6-8). Since ($^{13}C_6$)benzene is available commercially at high enrichment ($\geq$ 99 atom % ^{13}C) and is relatively inexpensive, we sought methods for the preparation of the four compounds selected (I-IV) which would most efficiently utilize this starting material.



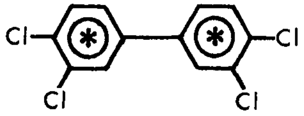
I

4-Chloro(1',2',3',4',5',6'-$^{13}C_6$)-biphenyl



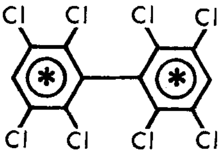
II

Decachloro($^{13}C_{12}$)biphenyl



III

3,3',4,4'-Tetrachloro($^{13}C_{12}$)biphenyl

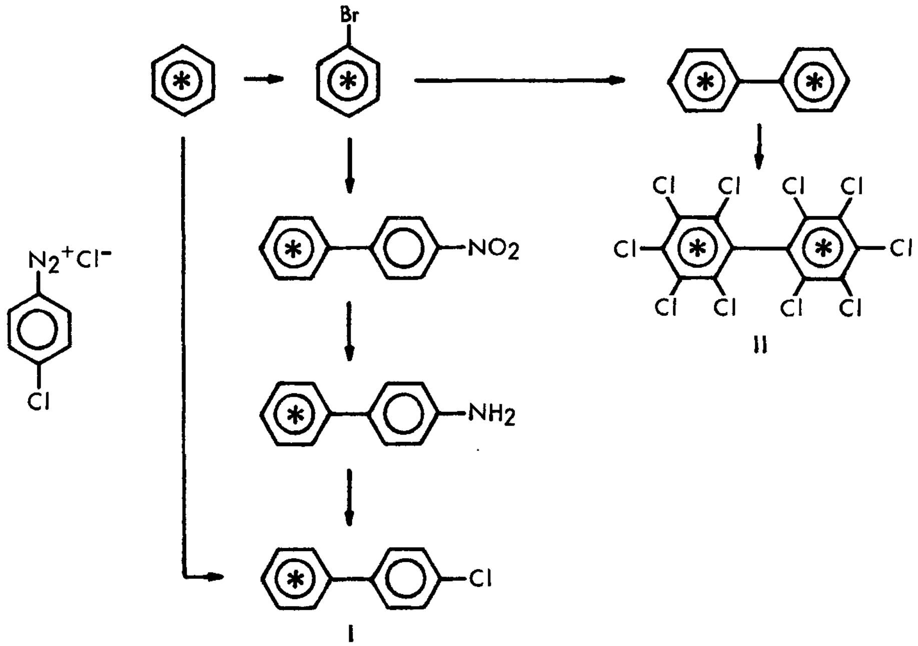


IV

2,2',3,3',5,5',6,6'-Octachloro-($^{13}C_{12}$)biphenyl

Scheme 1 summarizes the syntheses chosen for 4-chloro(1',2',3',4',5',6'-$^{13}C_6$)biphenyl (Compound I) and decachloro($^{13}C_{12}$)biphenyl (Compound II). Bromo-($^{13}C_6$)benzene was prepared by the method of Harrison et al. (9) using potassium bromate in acidic solution. Direct conversion of this intermediate to Compound I using the palladium-catalyzed coupling of the derived ($^{13}C_6$)phenyl zinc chloride with p-chloroiodobenzene by the method of Negishi et al. (10) gave a product contaminated with several percent of 4,4'-dichlorobiphenyl, removable only with difficulty from the desired compound.

Scheme 1



The same coupling using p-iodonitrobenzene, however, provided 4-nitro-(1',2',3',4',5',6'-$^{13}C_6$)biphenyl in high purity; catalytic reduction of this compound gave the mildly air-sensitive 4-amino(1',2',3',4',5',6-$^{13}C_6$)biphenyl in 42% overall yield from bromo($^{13}C_6$)benzene. Although 70-80% yields of Compound I could be obtained from the amino precursor by means of the Doyle et al., modification (11) of the Sandmeyer reaction originally described for these compounds (12), the product invariably contained several percent ($^{13}C_6$)biphenyl, which could be removed only by several recrystallizations resulting in large losses of product. More satisfactory purity but lower yields were obtained by use of more conventional Sandmeyer conditions, which resulted after one recrystallization in 129 mg (28% yield) of Compound I displaying a ≧ 99% purity by GC/FID (flame ionization detection) and by total ion current GC/EIMS.

The overall yield of the above synthesis (ca. 10%) in four steps from ($^{13}C_6$)benzene, however, was no better than we had obtained in trial runs of the one-step preparation of 4-chlorobiphenyl by variations of the Gomberg reaction (13) (p-chlorobenzenediazonium chloride and benzene). Therefore, for preparation of a 1-g quantity of Compound I, the latter direct method was used. An aqueous solution of the diazonium salt was reacted with ($^{13}C_6$)benzene in the presence of 18-crown-6. The unreacted ($^{13}C_6$)benzene, isolated by vacuum distillation, was treated similarly in three more reaction cycles. Workup and purification of the combined products provided 1.04 g of Compound I with a purity equivalent to that of the product of the smaller scale synthesis.

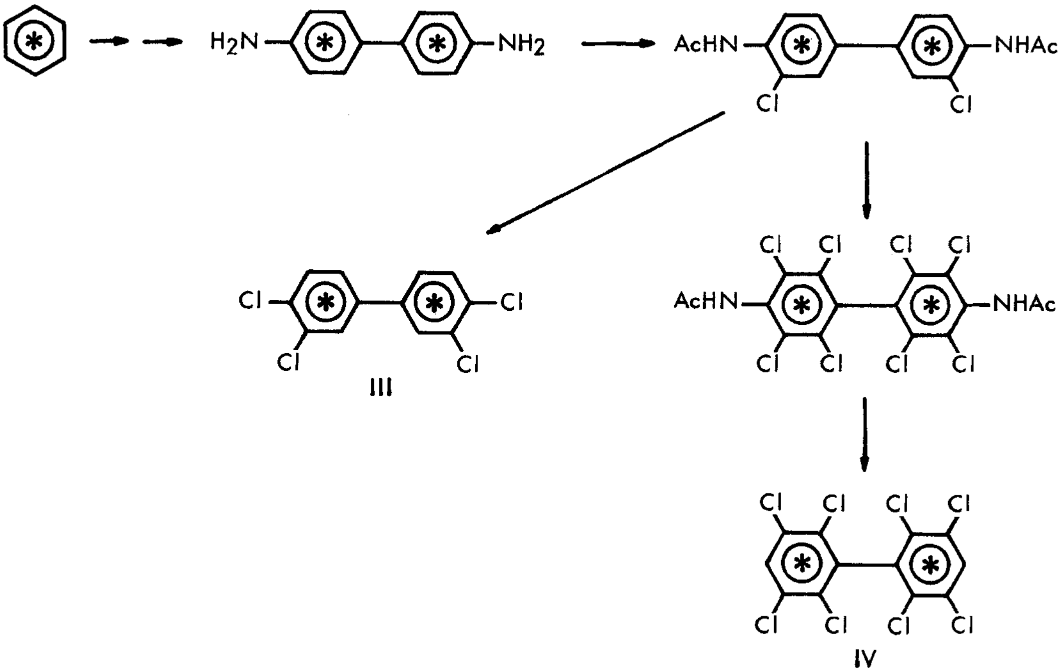
A 1.4 g sample of decachloro($^{13}C_{12}$)biphenyl (Compound II) of ≧ 98% purity was prepared following the route shown in Scheme 1. Bromo($^{13}C_6$)benzene was converted to ($^{13}C_{12}$)biphenyl in 90% yield using the thallium(I) bromide induced coupling of the aryl Grignard reagent as described by McKillop et al. (14). Perchlorination of biphenyl with reagent BMC (15) has been reported (16) to give decachlorobiphenyl in high yield, although the details of the procedure have not been described. Application of the originally described general chlorination procedure (15) to ($^{13}C_{12}$)biphenyl gave Compound II in excellent yield, although it was necessary to subject the initial product to a second chlorination in order to minimize lower chlorinated biphenyls in the crude product and thus simplify purification. Reagent BMC was found to be far superior to antimony pentachloride (17) for the chlorination of biphenyl.

The preparation of 3,3',4,4'-tetrachloro($^{13}C_{12}$)biphenyl (Compound III) was accomplished according to previously described methods as outlined in Scheme 2. Nitration of ($^{13}C_6$)benzene according to the method of Spitzer and Stewart (18) followed by reduction to hydrazo($^{13}C_{12}$)benzene and benzidine rearrangement (19) afforded ($^{13}C_{12}$)benzidine in good yield and high purity. The latter compound was transformed as previously described (19) for unlabeled material into 3,3'-dichloro($^{13}C_{12}$)benzidine. Conversion to Compound III was accomplished using the Doyle et al. modification (11) of the Sandmeyer reaction. The small amount of contaminating trichloro($^{13}C_{12}$)biphenyl, formed apparently by competing reductive deamination processes, was removed by careful recrystallization from hexane.

Previously described syntheses of 2,2',3,3',5,5',6,6'-octachlorobiphenyl (unlabeled Compound IV) include both the Ullman coupling of 2,3,5,6-tetrachloroiodobenzene (20) and the reductive deamination of octachlorobenzidine (12). Binns and Suschitzky (21) have reported, however, that reaction of decachlorobiphenyl with excess lithium aluminum hydride (LAH) or with n-butyllithium followed by water quench afforded the desired octachloro product in 70-80% yield. Since decachloro($^{13}C_{12}$)biphenyl (Compound II) was readily accessible, as described above, the latter method was investigated first. In contrast to the results reported (21), we found that decachlorobiphenyl, when reacted with LAH or n-butyllithium/water under the described conditions or variations thereof, gave complex product mixtures (judged by GC/FID analysis using appropriate standard samples) containing no more than 60% of the desired octachloro congener. Since purification of such complex mixtures would have been extremely difficult, other approaches were investigated.

Octachlorobenzidine has been previously prepared by the reaction of decachlorobiphenyl with ammonia at high temperature and pressure (280°, > 6,000 psi, 5 h) (22). Milder conditions (100°) compatible with more conventional pressure-reaction vessels, even with reaction times of up to 1 week, however, resulted in negligible yields of desired product in our hands.

Scheme 2



A second reported preparation of octachlorobenzidine involved chlorination of 2,2',6,6'-tetrachlorobenzidine with chlorine gas (12), and this suggested that perchlorination of benzidine or certain derivatives might be feasible. A preliminary trial reaction of diacetylbenzidine with the BMC-chlorination reagent, already successfully used in the preparation of decachloro($^{13}C_{12}$)biphenyl (Compound II), indicated that perchlorination of diacetylbenzidine might be achieved under prolonged or vigorous conditions. This was demonstrated subsequently by the synthesis of a small (*ca*. 100 mg) quantity of 2,2',3,3',5,5',6,6'-octachloro($^{13}C_{12}$)biphenyl (Compound IV) via perchlorination of a sample of partially chlorinated diacetyl($^{13}C_{12}$)benzidine which was a by-product of the tetrachloro($^{13}C_{12}$)biphenyl synthesis. However, the more efficient procedure ultimately used for the preparation of 1.09 g of > 99% pure Compound IV involved, as shown in Scheme 2, initial dichlorination of diacetyl($^{13}C_{12}$)benzidine (12). Subsequent perchlorination by means of the BMC reagent, hydrolysis, and careful purification by recrystallization provided a 34% yield [from N,N'-diacetyl($^{13}C_{12}$)-benzidine] of octachloro($^{13}C_{12}$)benzidine. Following reductive deamination (23) and purification by chromatography and crystallization, 1.09 g of > 99% pure Compound IV was obtained.

EXPERIMENTAL

($^{13}C_6$)Benzene of > 99 atom % purity was purchased from Cambridge Isotope Laboratories, Inc., Cambridge, Massachusetts. Standard samples of 4-chlorobiphenyl (unlabeled Compound I); decachlorobiphenyl (unlabeled Compound II); 3,3',4,4'-tetrachlorobiphenyl (unlabeled Compound III); and 2,2',3,3',5,5',6,6'-octachlorobiphenyl (unlabeled Compound IV) were purchased from Ultra Scientific, Inc., Hope, Rhode Island.

Capillary GC/EIMS spectra were run using a Finnigan 4023 GC/MS with an INCOS 2400 data system, J&W on-column injection, and Durabond-5 15 m fused silica capillary column programmed from 110° to 280° at 10°/min after a 2-min initial delay. The spectrometer was scanned from m/z 95 to 550 in 1 s at 70 eV. GC/FID analyses were performed on a Varian Model 3700 gas chromatograph with a Shimadzu CR1B integrator. Columns and conditions were as follows: GC/FID System 1 - 1.8 m x 2 mm ID glass column packed with 20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport; and GC/FID System 2 - 1.8 m x 2 mm ID glass column packed with 3% SP-2250 on 100/120 Supelcoport, 100° to 270° at 8°/min after initial 3-min delay.

UV-visible spectra were recorded on a Varian SuperScan 3 UV/vis spectrophotometer, and infrared spectra were recorded on a Beckman Acculab 1 instrument. Melting points were uncorrected.

Bromo($^{13}C_6$)benzene

This compound was prepared from 6.77 g of ($^{13}C_6$)benzene by the method of Harrison et al. (9) except that the product was purified by distillation. The yield was 9.0 g (68%) of material with ≧ 95% purity (GC/FID, System 1).

4-Nitro(1',2',3',4',5',6'-$^{13}C_6$)biphenyl

A solution of ($^{13}C_6$)phenyl lithium prepared from 1.57 g (9.64 mmoles) bromo($^{13}C_6$)benzene and 0.167 g (24.0 mmol) lithium wire in 10 mL diethyl ether (11) was transferred by double-tipped needle into a solution of 1.36 g (10.0 mmol) freshly fused zinc chloride in 20 mL anhydrous tetrahydrofuran (THF). In a separate flask, a suspension of dichlorobis(triphenylphosphine)palladium(II) (0.22 g, 0.313 mmol) in 10 mL THF was treated with 0.67 mL of 1 M diisobutylaluminum hydride in hexane, under an inert atmosphere. To this suspension was added 4-iodonitrobenzene (1.99 g, 8.0 mmol in 25 mL THF), followed by the ($^{13}C_6$)-phenyl zinc chloride solution. The mixture was stirred 1 h at room temperature and the reaction quenched by the addition of a dilute HCl solution. Workup by ether extraction, column chromatographic purification of the crude product (silica gel, hexane/acetone 19:1), followed by recrystallization from ethanol, provided 952 mg (48% yield) 4-nitro(1',2', 3',4',5',6'-$^{13}C_6$)biphenyl as large yellow needles, mp 110.5°-112° [literature (24) for unlabeled material: 113.7°].

4-Amino(1',2',3',4',5',6'-$^{13}C_6$)biphenyl

4-Nitro(1',2',3',4',5',6'-$^{13}C_6$)biphenyl (614 mg, 3.0 mmol), dissolved in 40 mL dry THF, was reduced with 1 atm H_2 at room temperature for 1.75 h in the presence of 126 mg 10% Pd/C. Filtration and evaporation of the filtrate provided an off-white solid, which was recrystallized from hexane to give 463 mg (88% yield) 4-amino(1',2',3',4',5',6'-$^{13}C_6$)biphenyl as white plates, mp 51°-53° [literature (25) for unlabeled material: 53°].

4-Chloro(1',2',3',4',5',6'-$^{13}C_6$)biphenyl (Compound I)

From 4-amino(1',2',3',4',5',6'-$^{13}C_6$)biphenyl. A 0.506 mL (4.62 mmol) portion of *t*-butylnitrite was added to a suspension of 780 mg (5.78 mmol) anhydrous $CuCl_2$ in 5 mL dry acetonitrile. The suspension was warmed to 65° under inert atmosphere, and 4-amino(1',2',3',4',5',6'-$^{13}Cl_6$)biphenyl (405 mg, 2.31 mmol) dissolved in 1.5 mL acetonitrile was added over a 15-min period. After an additional 1 h reaction time, the reaction was diluted with 6 N HCl and extracted four times with ether. The combined organics were washed with water and then with $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated <u>in vacuo</u>. The residue was purified by column chromatography (silica gel, hexane). The product was recrystallized from hexane at -78° and then sublimed at 75° and 0.1 mm to yield 129 mg 4-chloro(1',2',3',4',5',6'-$^{13}C_6$)biphenyl (Compound I) as white plates, mp 74.5°-76° [literature (26) for unlabeled material: 76°-78°]. The material's purity was 99.0% by GC/FID (System 2); GC/EIMS, m/z (%): 196 (33.4), 195 (9.9), 194 (100.0), 193 (10.7), 159 (14.2), 158 (58.6), 157 (19.9), 156 (9.4); UV/vis (95% ethanol): λ_{max} 252 (ε = 20,600); and IR ($CHCl_3$): 3055, 1490, 1454, 1092, 1016, 833 cm^{-1}.

<u>From ($^{13}C_6$)benzene</u>. A solution of 4-chlorobenzenediazonium chloride prepared from 4-chloroaniline (3.79 g, 29.7 mmol) and sodium nitrite (2.28 g, 33 mmol) in 30 mL 3 N HCl at 0° was added over a 2-h period to the two-phase mixture of ($^{13}C_6$)benzene (5.0 g, 59.5 mmol), 18 mL 4 N NaOH and 5 mg 18-crown-6 with vigorous stirring. After the addition was complete, the unreacted ($^{13}C_6$)-benzene was separated by vacuum transfer at room temperature, and the nonvolatile organic reaction products retained. The recovered ($^{13}C_6$)benzene was distilled (yield 3.0 g) and the reaction with 4-chlorobenzenediazonium chloride was repeated on a scale proportional to the amount of recovered ($^{13}C_6$)benzene. The process was repeated twice more, and the reaction products from all runs were combined and steam distilled, providing 1.8 g of crude 4-chloro(1',2',3',4',5',6'-$^{13}C_6$)biphenyl (Compound I) as a yellow solid (87% purity by GC/FID, System 2). The purity was increased to 99% (GC/FID, System 2) by column chromatography, yielding 1.04 g (9% yield) material whose physicochemical characteristics matched those of the product of the other synthesis.

<u>($^{13}C_{12}$)Biphenyl</u>

The synthesis was conducted essentially by the method of McKillop et al. (14) for unlabeled material. Thus, 2.119 g (13.0 mmol) of bromo($^{13}C_6$)benzene was converted to the Grignard reagent in THF; the solution was added to thallium(I) bromide (7.38 g, 26 mmol) in 6 mL benzene and the mixture refluxed for 3 h. Workup and recrystallization from methanol/water (4:1) provided 904 mg (90% yield) of ($^{13}C_{12}$)biphenyl as white plates, mp 67.5°-69° [literature (27) for unlabeled material: 69°-71°). GC/FID analysis (System 1) indicated a purity of > 99%.

Decachloro($^{13}C_{12}$)biphenyl (Compound II)

In a method similar to that of Ballester et al. (15), ($^{13}C_{12}$)biphenyl (719.3 mg, 4.33 mmol) dissolved in sulfuryl chloride (20 mL) and sulfur monochloride (353 mg) was added over 20 min to a refluxing solution of aluminum chloride (178 mg, 1.33 mmol) in 50 mL sulfuryl chloride. After 5-1/2 h reflux, the small amount of solution remaining from sulfuryl chloride decomposition was stripped of volatiles in vacuo and the residue treated with dilute HCl. Extraction with chloroform and washing of the organic solution sequentially with dilute NaOH and HCl, drying, and evaporating (in vacuo) provided a crude product of ca. 96% purity (GC/FID, System 2).

Reexposure of this product to the above chlorination conditions and purification of the material by column chromatography (silica gel, hexane) and recrystallization from benzene provided 1.4 g (63% yield) decachloro($^{13}C_{12}$)biphenyl (Compound II) of 98.4% purity by GC/FID (System 2) and > 99% by GC/EIMS chromatogram, m/z (%): 512 (70.7), 510 (100.0), 508 (75.1), 440 (63.1), 438 (57.4), 368 (66.0), 255 (50.6), 221 (50.4), 220 (89.5), 219 (84.2), 185 (60.7), 184 (76.4), 183 (53.4), 148 (58.6); UV (THF), λ_{max} (ε): 289 (1090), 299 (1155); and IR ($CHCl_3$): 1322, 1302, 1290 cm^{-1}.

N,N'-Diacetyl-3,3'-dichloro($^{13}C_{12}$)benzidine and N,N'-Diacetyl-polychloro($^{13}C_{12}$)-benzidine

($^{13}C_{12}$)Benzidine (4.87 g, 58.0 mmol) was nitrated by the method of Spitzer and Stewart (18), and this product was converted in three more steps by the method of Duncan et al. (19) to provide 4.55 g (55% overall yield) of N,N'-diacetyl-3,3'-dichloro($^{13}C_{12}$)benzidine of ≧ 95% purity by thin-layer chromatography [silica gel 60, benzene/acetone (2:1), R_f = 0.38] by crystallization from the chlorination reaction mixture. Isolated as by-product from the chlorination was a total of 1.40 g of N,N'-diacetyl-polychloro($^{13}C_{12}$)benzidine as an amorphous solid. Both products were used in subsequent steps without further purification.

3,3'-Dichloro($^{13}C_{12}$)benzidine

A 2.74 g (8.1 mmol) portion of N,N'-diacetyl-3,3'-dichloro($^{13}C_{12}$)benzidine was hydrolyzed in ethanol/aqueous HCl by the method of Duncan et al. (19) to provide 2.00 g (93% yield) of 3,3'-dichlorobenzidine, mp 130°-132° [literature (28) for unlabeled material: 133°], which was used directly in the next step.

3,3',4,4'-Tetrachloro($^{13}C_{12}$)biphenyl (Compound III)

A solution of sodium nitrite (349 mg, 5.05 mmol) in 2 mL water was added dropwise to a stirred solution of dichloro($^{13}C_{12}$)benzidine (478.7 mg, 1.81 mmol) in 4 mL 16% HCl at 0°. The resulting mixture was stirred at 0° for 5 min, and then was added dropwise to a solution of cuprous chloride (429 mg, 432 mmol) in 3 mL concentrated HCl. The resulting suspension was stirred at 0° for 0.5 h, and then at room temperature for 1 h. The solid collected by filtration was dried under vacuum and purified by column chromatography (alumina, hexane) to provide 401 mg crude 3,3',4,4'-tetrachloro($^{13}C_{12}$)biphenyl (Compound III) of 95% purity by GC/FID (System 2). This was combined with portions of product from two other runs and recrystallized from ethanol, yielding 1.5 g (50% yield) of product with 98.4% purity by GC/FID (System 2), mp 176°-177°C [literature (13): 171°]; GC/EIMS, m/z (%): 308 (10.1), 306 (46.3), 304 (100.0), 303 (16.0), 302 (78.3), 301 (12.5), 234 (32.5), 232 (51.6), 231 (10.2), 197 (10.6), 196 (14.9), 162 (16.4); UV (95% EtOH), λ_{max} (ε): 261 (23,500); and IR (nujol): 1360, 1324, 1100, 988, 862, 800, 720 cm^{-1}.

Octachloro($^{13}C_{12}$)benzidine

Using the procedure of van Roosmalen (12), chlorine gas was bubbled through a suspension of 5.3 g (18.9 mmol) N,N'-diacetyl($^{13}C_{12}$)benzidine in refluxing acetic acid. After 4 h, chlorine introduction was stopped and the reaction mixture was allowed to cool. The precipitate was collected by filtration, and the filtrate was diluted to 550 mL with water and filtered again. The two portions of crystalline product were combined and dried, yielding 7.4 g white solid.

This material was suspended in 560 mL of sulfuryl chloride and the mixture heated to reflux while adding sulfur monochloride (14.1 g, 104 mmol). A solution of aluminum chloride (7.12 g, 53 mmol) in 50 mL sulfuryl chloride was added dropwise over 10-12 min, and the resulting solution was refluxed for 41 h with the addition of 550 mL more sulfuryl chloride as needed to maintain the solution of the reactants and products. Workup of the reaction was begun by treatment with crushed ice, and hydrolysis was accomplished by the addition of H_2SO_4 and stirring at 85° for 1 h. Cooling, dilution with water, ethyl acetate extraction, drying, and evaporation provided the product as a crude solid. Column chromatographic purification (silica gel, methylene chloride) yielded 8.1 g of light colored solid. Two recrystallizations from hexane were required for removal of small quantities of incompletely chlorinated by-products, and resulted in 3.13 g (34.4% yield) of octachloro($^{13}C_{12}$)benzidine. Measurement of total ion current in the GC/EIMS showed the product to be of $\geqq$ 98.5% purity.

2,2',3,3',5,5',6,6'-Octachloro($^{13}C_{12}$)biphenyl (Compound IV)

A solution of octachloro($^{13}C_{12}$)benzidine (1.5 g, 3.18 mmol) in 12 mL dimethyl formamide was added dropwise with stirring to freshly distilled _t_-butylnitrite (3.99 g, 38.7 mmol) under an argon atmosphere. After nitrogen evolution ceased (20 min), volatiles were removed _in vacuo_ and the resulting solid was purified by column chromatography (silica gel, hexane) to provide 312 mg white crystalline product. This was combined with the product of a similar run and recrystallized from absolute ethanol to give 1.09 g (37.8% yield) octachloro($^{13}C_{12}$)biphenyl of > 99% purity by GC/EIMS; mp 159.5°-160.5° [literature (7) for unlabeled material: 161°]; GC/EIMS, m/z (%): 444 (60.9), 442 (100.0), 440 (97.8), 438 (41.5), 372 (51.6), 370 (65.9), 368 (39.9), 300 (37.7), 186 (42.4), 185 (55.0), 150 (38.6), 149 (44.1); UV (95% EtOH), λ_{max} (ε): 286 (1935), 295 (2045); and IR ($CHCl_3$): 1360, 1278, 1153, 1142, 1022, 860 cm^{-1}.

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