Table V. Alkylation of other Nitriles

Registry no.	Nitriles[a]	% yield of monoalkylation
22364-68-7	o-methylphenylacetonitrile	60[b]
3215-64-3	2,6-Dichlorophenylacetonitrile	25[b]
124-12-9	n-Octylnitrile	0
766-05-9	Cyclohexylnitrile	0

[a] Using 4 g of Dowex 2-X4, 20–50 mesh, and a reaction time of 10 h for a reaction temperature of 70 °C. [b] The dialkylation yield found to be about 1%.

(2) Triphase Catalysis. Nitrile (0.1 mol), 0.1 mol of n-butyl bromide, 40 cm³ of NaOH (50 or 10% by weight), and x g of resin (see Table II) were stirred vigorously at 70 °C for x h. At the end of the reaction the resin was removed by filtration, and the organic layer was separated and treated as usual.

(3) Use of an Alkyl Iodide. The same conditions as above were used, with 4 g of Dowex 1-X8, at a temperature of 70 °C for 10 h.

(4) Determination of the Equivalence of the Catalytic Action of the Salts and Resin. Dowex 1-X8 resin (2 g) was stirred for 30 min with 40 cm³ of 50% (by weight) NaOH. After this time, the resin was removed by filtration and washed with distilled water (no reaction to phenolphthalein was observed). The resin was then titrated with dilute hydrochloric acid (helianthine used as indicator).

(5) Structure of the Products. The identification of the products has been carried out by GLC/MS (Varian MAT 111). Monoalkylated products: $C_{12}H_{15}N$ 173, 158, 144, 130, 129, 118, *117*, 116, 91, 90, 77, 57, 41; $C_{13}H_{17}N$ 187, 144, 143, 132, *131*, 130, 105, 104, 103, 91, 77, 65, 63, 57, 41; $C_{12}H_{13}NCl_2$ 245, 243, 241, 208, 206, 189, *185*, 182, 150, 114, 57, 41; $C_{10}H_{11}N$ 145 (45.8), 118 (8.3), 117 (100), 116 (87.5), 91 (41.6), 90 (29.1), 89 (20.8), 78 (4.1), 77 (4.1), 63 (8.3), 51 (8.3), 39 (6.2). Dialkylated product: $C_{16}H_{23}N$ 229, 187, *173*, 172, 158, 145, 130, 118, 117, 116, 91, 77, 58.

Registry No.—Butyl bromide, 109-65-9; ethyl iodide, 75-03-6; phenylacetonitrile, 140-29-4; α-butylphenylacetonitrile, 3508-98-3; α-butyl-o-methylphenylacetonitrile, 63866-33-1; α-butyl-2,6-dichlorophenylacetonitrile, 58830-65-2; α-ethylphenylacetonitrile, 769-68-6; α,α-dibutylphenylacetonitrile, 3508-99-4.

References and Notes

(1) S. L. Regen, *J. Am. Chem. Soc.*, **97**, 5956 (1975).
(2) S. L. Regen, *J. Am. Chem. Soc.*, **98**, 6270 (1976).
(3) E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.*, **13**, 170 (1974).
(4) A. W. Herriott and D. Picker, *J. Am. Chem. Soc.*, **97**, 2345 (1975).
(5) C. M. Starks, *J. Am. Chem. Soc.*, **95**, 3613 (1973).
(6) G. Cainelli and F. Manescalchi, *Synthesis*, 723 (1975).
(7) A. Bernardus, Petrolite Corp., U.S. Patent 3 904 625 (Sept 1975).
(8) J. Dockx, *Synthesis*, 441 (1973).
(9) D. L. Rakhmankulov, V. R. Melikyan, and S. S. Zlotska, *Khim. Tekhnol. Elementoorg. Soedin. Polim.*, 903 (1975).
(10) N. Yoshio, *Yuki Gosei Kagaku Kyokai Shi*, 903 (1975).
(11) G. Gelbard and S. Colonna, *Synthesis*, 113 (1977).
(12) M. Makosza, "Modern Synthetic Methods, Naked Anions", Phase-Transfer Conference Paper, International Workshop on Modern Synthetic Methods, Rolf Scheffold, Ed., University of Bern, 1976.
(13) M. Makosza, personal communication.
(14) According to the manufacturer of the resins used, the complete name for each resin will include: (1) type, i.e., Dowex 1, 2, 21K, Dowex 50. (2) "X number" or percent divinylbenzene, i.e., X8. The Dowex resins used are based on styrene divinylbenzene copolymer. Sulfonation of these copolymers with sulfuric acid yields strong cation resin, while "amination" with amines yields anion resins. (3) Mesh size, i.e., 20–50 mesh (based on U.S. standard screen). (4) Ionic form, i.e., Cl⁻. Dowex 1, Dowex 2, Dowex 11 and 21K resins are strong-base anion-exchange resins. All incorporate a quaternary ammonium functionality. Dowex 1, Dowex 11, and Dowex 21K resins are type 1 resins. In type 1 resins the four substituents on the nitrogen atom are a polymeric benzyl and three methyl groups. Dowex 2 resin is a type 2 resin in which one of the methyl groups is replaced by an ethanol group. Type 1 and type 2 resins differ primarily in their affinities for the hydroxide ion relative to other anions, and in chemical stability. Type 2 resins are more efficiently converted to the hydroxide form than type 1 resins, but the type 1 resins are inherently more stable chemically especially in the hydroxide form.
(15) H. J. M. Dou, P. Hassanaly, R. Gallo, J. Metzger, to be submitted for publication.

Improved Syntheses of Bis(pentafluorophenyl)acetylene, (Pentafluorophenyl)phenylacetylene, and Hexakis(pentafluorophenyl)benzene

Robert G. Gastinger, Edward F. Tokas, and Marvin D. Rausch*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

Received May 31, 1977

During the course of some recent investigations concerning the reactions of organometallic complexes with partially and completely halogenated diarylacetylenes,[1] we have been required to synthesize various quantities of bis(pentafluorophenyl)acetylene (1) and (pentafluorophenyl)phenylacetylene

$$C_6F_5C\equiv CC_6F_5 \qquad C_6F_5C\equiv CC_6H_5$$

1   **2**   **3**
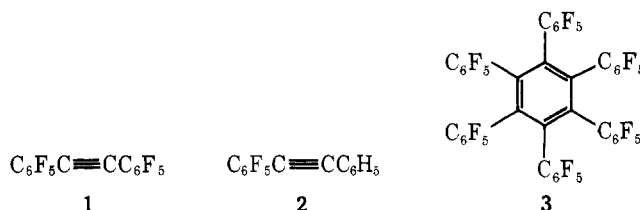
(2). As a result, we have developed reliable experimental procedures based on the commercially available reagent bromopentafluorobenzene, from which reasonable quantities of these acetylenes can be obtained. Moreover, a new synthesis of hexakis(pentafluorophenyl)benzene (3) is also presented.

Several synthetic routes to 1 have been reported.[2-8] Many of these, however, are not convenient for the production of practical amounts of this acetylene. Birchall et al.[2] have described a useful but potentially hazardous preparation of 1 in 56% yield by the cobalt-catalyzed reaction of pentafluorophenylmagnesium bromide with diiodoacetylene. A major drawback of this method involves the use of diiodoacetylene, a compound well known for its thermal and mechanical instability.[9]

Perhaps the most useful preparation of bis(polyhaloaryl)acetylenes such as 1 has been suggested by Gilman and co-workers.[6] Their method utilizes the reaction of polyhaloarylcopper reagents or their complexes with polyhaloethylenes or polyhaloethanes. The use of this method for the synthesis of 1 has been alluded to several times in the literature, but unfortunately no detailed experimental procedures have ever been reported.[7,8] The preparation of 1 presented here is therefore based upon the original communication of Gilman et al.[6] and consists of the reaction of pentafluorophenylcopper, formed from pentafluorophenylmagnesium bromide and cuprous iodide, with tetrabromoethylene.

$$C_6F_5Br \xrightarrow[\text{(2) CuI}]{\text{(1) Mg, THF}} C_6F_5Cu \xrightarrow[\Delta]{C_2Br_4} 1$$
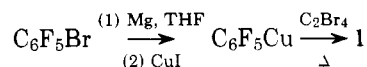
Of the several reported procedures for the synthesis of 2,[3,10-13] the most useful involves the reaction of iodopentafluorobenzene with phenylethynylcopper. A wide range of conditions, i.e., solvent, reaction temperature, and time, has been employed, and the yields vary from 20 to 74%.[3,11,12] Under similar conditions the reaction of bromopentafluorobenzene and phenylethynylcopper gave both lower yields of 2 as well as a more difficult purification. In the present synthesis of 2, we have found that by reversing the functionality of the aforementioned reagents, i.e., using pentafluorophenylcopper and phenyliodoacetylene, good yields of 2 can be conveniently obtained. This method thus eliminates the purchase or tedious preparation[11] of iodopentafluorobenzene.

© 1978 American Chemical Society

Table I. Cyclic Trimerization of Bis(pentafluorophenyl)-acetylene (1) with Bis(tetracarbonylcobalt)mercury

Method	Time, min	Temp, °C	% Yield[a] 3	% Yield[a] 4
A	25	230–240	57	Trace
B	30	245–250	49	4.5
C	270	101	7	0

[a] Based on unrecovered 1.

$$C_6F_5Cu + IC{\equiv}CC_6H_5 \xrightarrow{Et_2O} 2$$
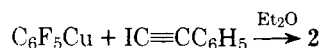
Hexakis(pentafluorophenyl)benzene (3) has been suggested for use as a high mass marker in mass spectrometry.[1a] It is not a readily available compound, however, and has only been obtained as a product in the reactions of various rhodium– and iridium–carbonyl complexes with 1.[1a,b,e] The best yields of this trimerization product (40–70%) resulted from the use of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$.[1a] More recent work in our laboratories has shown that the yields of 3 produced in this reaction fluctuate widely and are often not reproducible. Moreover, $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ is an expensive reagent for use in this synthesis.

The cyclic trimerization of acetylenes in the presence of metal carbonyls is a well-known phenomenon in organometallic chemistry.[14] Employment of cobalt–carbonyl complexes such as $Co_2(CO)_8$,[14] $Hg[Co(CO)_4]_2$,[15] and $(\eta^5\text{-}C_5H_5)Co(CO)_2$[16] as reagents have produced good results for many disubstituted acetylenes. In an attempt to devise a more convenient and reproducible synthesis of 3, the reaction of 1 with bis(tetracarbonylcobalt)mercury was investigated.

$$1 + Hg[Co(CO)_4]_2 \xrightarrow{\Delta} 3 +$$

4
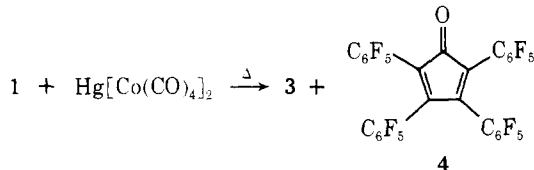
Several methods were examined and the results are summarized in Table I. Method A consists of a melt-phase reaction in which the internal pressure of the reaction vessel is maintained at atmospheric pressure. This procedure gave the best overall results. Method B is a melt-phase reaction performed in a sealed tube, while method C consists of refluxing the reagents in dioxane.

Both methods A and B gave good yields of the trimer 3. Method B, however, also produced small but isolable amounts of tetrakis(pentafluorophenyl)cyclopentadienone (4). The formation of this carbonyl insertion product is probably enhanced by the large internal CO pressure generated in the sealed tube. Method C, while the method of choice for many other disubstituted acetylenes,[15] gave the poorest yield of 3.

Experimental Section

All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Cuprous iodide[17] and bis(tetracarbonylcobalt)mercury[18,19] were synthesized using published procedures. Tetrahydrofuran (THF) and diethyl ether were dried and distilled over sodium–benzophenone under nitrogen before use. Infrared spectra were recorded on a Beckman IR-10 instrument. Mass spectra were determined on a Perkin-Elmer-Hitachi RMU-6L instrument. Bromopentafluorobenzene and tetrabromoethylene were used as purchased from Bristol Organics, Ltd., Bristol, England, and the Columbia Organic Chemicals Co., Charleston, S.C., respectively. Melting points are uncorrected and were taken in open capillaries.

Preparation of Bis(pentafluorophenyl)acetylene (1). A 250-mL three-necked flask fitted with a magnetic stirrer, a nitrogen inlet valve, a condenser with a mercury overpressure valve, and a pressure-equalizing addition funnel was evacuated and flushed with nitrogen. Into this flask were placed dry magnesium turnings (2.43 g, 0.10 mol) and 35 mL of THF. A solution of bromopentafluorobenzene (24.7 g, 0.10 mol) in 50 mL of THF was added dropwise at such a rate as to promote a gentle reflux. After the addition was complete, the reaction mixture was refluxed for 20 min.

The reaction mixture was then cooled to 0 °C, freshly prepared cuprous iodide[1] (21.0 g, 0.11 mol) and 20 mL of THF (to facilitate stirring) were added, and the temperature was maintained for 3 h. A solution of tetrabromoethylene (11.6 g, 0.034 mol) in 50 mL of THF was then added and the mixture refluxed for 40 h.[20] The reaction mixture was cooled and hydrolyzed with 60 mL of water, and the THF was removed by means of a water aspirator. The residue was extracted with three 100-mL portions of ether. The extracts were combined and then dried over anhydrous magnesium sulfate. The solution was filtered and the solvent was removed.

Sublimation of the resulting brown residue at 50 °C (10^{-2} Torr) produced small amounts of unreacted tetrabromoethylene. Further sublimation at 90 °C (10^{-2} Torr) gave 8.6 g (66%) of 1: mp 108–109 °C. Recrystallization from hexane or methanol afforded 6.4 g (52%) of product: mp 121–122 °C (lit.[2] 123–123.5 °C).

Preparation of (Pentafluorophenyl)phenylacetylene (2). Pentafluorophenylcopper was prepared in diethyl ether as indicated above from pentafluorophenylmagnesium bromide, formed from magnesium (0.54 g, 0.022 mol), 70 mL of diethyl ether, bromopentafluorobenzene (5.48 g, 0.022 mol) and cuprous iodide (4.18 g, 0.022 mol).

Simultaneously,[21] to a solution of phenylacetylene (2.24 g, 0.022 mol) in 40 mL of diethyl ether which had been cooled in a dry ice-acetone bath was added 9.8 mL of a 2.25 M n-butyllithium–hexane solution at such a rate to maintain the temperature at −70 °C. To this stirred solution was added iodine (5.58 g, 0.022 mol) in 30 mL of ether dropwise until a faint red color persisted. Throughout the addition the temperature was held at −70 °C.

The phenyliodoacetylene solution was then transferred under nitrogen to a jacketed addition funnel maintained at −70 °C and added dropwise over a period of 20 min to the pentafluorophenylcopper reagent at 0 °C. The reaction mixture was then allowed to stir for 30 min each at 0 °C and at room temperature. The reaction mixture was subsequently hydrolyzed with 150 mL of 6% hydrochloric acid and washed with two 250-mL portions of water, 5% sodium bicarbonate solution, and water in that order. The resulting ether solution was then decolorized with charcoal, dried over magnesium sulfate, and filtered. To the solution was added silica gel (30–40 g) and the solvent was removed. The coated silica was placed on a silica gel column (4 × 50 cm) which had been packed dry. Elution of this column with ca. 1 L of hexane produced 5.2 g of the acetylene 2. Recrystallization from hexane yielded 4.9 g (82%) of 2, mp 92–93 °C (lit.[11] 93–94 °C; lit.[12] 105–106 °C).

Reaction of Bis(pentafluorophenyl)acetylene (1) and Bis(tetracarbonylcobalt)mercury. Method A. Bis(pentafluorophenyl)acetylene (1.08 g, 3.02 mmol) and bis(tetracarbonylcobalt)-mercury (0.100 g, 0.184 mmol) were added to a Schlenk tube (4 × 15 cm) fitted with a mercury overpressure valve and which had been evacuated and flushed with nitrogen. The Schlenk tube was heated to 230–240 °C via a Wood's metal bath for 25 min. The tube was then cooled and the contents extracted with methylene chloride and filtered. The extraction was continued until the filtrate remained colorless. The residual gray-black solid was dried and sublimed at 205–210 °C (10^{-3} Torr) to give 0.446 g (41%, 57% based on unrecovered 1) of a white solid identified by infrared and mass spectrometry and by comparison to an authentic sample[1a] as hexakis(pentafluorophenyl)benzene (3).

The solvent was removed from the filtrate and the residue sublimed at 90 °C (10^{-2} Torr) to give 0.302 g (28% recovery) of unreacted 1. TLC analysis of the residue from the sublimation indicated the presence of trace amounts of tetrakis(pentafluorophenyl)cyclopentadienone (4) (vide infra).

Method B. Bis(pentafluorophenyl)acetylene (1.70 g, 4.75 mmol) and bis(tetracarbonylcobalt)mercury (0.100 g, 0.184 mmol) were introduced into a thick-walled (3 mm) Pyrex tube (2 × 12.5 cm) and the tube was sealed under vacuum. The sealed tube was then immersed in a Wood's metal bath maintained at 245–250 °C for 30 min, allowed to cool, and cautiously opened. The reaction mixture was extracted with methylene chloride and filtered. The extraction was continued until the filtrate remained colorless. The residual gray-black solid was dried and sublimed at 205–210 °C (10^{-3} Torr) to give 0.396 g (23%, 49% based on unrecovered 1) of 3.

The solvent was removed from the orange filtrate and the residue

sublimed at 90 °C (10^{-2} Torr) to give 0.890 g of unreacted **1** (52% recovery). A red solid remained which was dissolved in methylene chloride. Alumina (1 g) was added, the solvent was removed in vacuo and the material was added to a dry alumina column (2 × 20 cm). Elution with benzene gave a red band. The solvent was removed and the residue was crystallized from chloroform to give 0.075 g (5%) of tetrakis(pentafluorophenyl)cyclopentadienone (**4**), which was identified by comparison to a known sample: mp 243–244 °C (lit.[2] 231–231.5 °C); M^+ 744 (mass spectrometry) (calcd: 744).

Method C. Bis(pentafluorophenyl)acetylene (1.00 g, 2.79 mmol) and bis(tetracarbonylcobalt)mercury (0.100 g, 0.184 mmol) were refluxed in 25 mL of dioxane for 4.5 h under nitrogen with magnetic stirring. The reaction mixture was cooled and filtered in air, and the residue was washed with methylene chloride to give small amounts of metallic mercury. The solvent was removed from the filtrate and the residue sublimed at 90 °C (10^{-3} Torr) to give 0.834 g (83% recovery) of unreacted **1**. Further sublimation of the residue at 200–205 °C (10^{-3} Torr) gave 0.012 g of **3** (1.2%, 7.2% based on unrecovered **1**).

Registry No.—**1**, 13551-43-2; **2**, 13509-88-1; **3**, 35525-35-0; **4**, 15070-92-5; bromopentafluorobenzene, 344-04-7; tetrabromethylene, 79-28-7; pentafluorophenylcopper, 18206-43-4; phenylacetylene, 536-74-3; phenyliodoacetylene, 932-88-7; bis(tetracarbonylcobalt)-mercury, 13964-88-0.

References and Notes

(1) (a) M. D. Rausch, P. S. Andrews, and S. A. Gardner, *Organomet. Chem. Synth.*, **1**, 289 (1970); (b) S. A. Gardner, P. S. Andrews, and M. D. Rausch, *Inorg. Chem.*, **12**, 2396 (1973); (c) S. A. Gardner, E. F. Tokas, and M. D. Rausch, *J. Organomet. Chem.*, **92**, 69 (1975); (d) R. G. Gastinger, M. D. Rausch, D. A. Sullivan, and G. J. Palenik, *J. Am. Chem. Soc.*, **98**, 719 (1976); (e) R. G. Gastinger, M. D. Rausch, D. A. Sullivan, and G. J. Palenik, *J. Organomet. Chem.*, **117**, 355 (1977).
(2) J. M. Birchall, F. L. Bowden, R. N. Haszeldine, and A. B. P. Lever, *J. Chem. Soc. A*, 747 (1967).
(3) R. Filler and E. W. Heffern, *J. Org. Chem.*, **32**, 3249 (1967).
(4) E. J. Soloski, W. E. Ward, and C. Tamborski, *J. Fluorine Chem.*, **2**, 361 (1971).
(5) R. D. Chambers, M. Clark, J. A. H. McBride, W. K. R. Musgrave, and K. C. Srivastava, *J. Chem. Soc., Perkin Trans. 1*, 125 (1969).
(6) A. E. Jukes, S. S. Dua, and H. Gilman, *J. Organomet. Chem.*, **12**, P44 (1968).
(7) A. F. Webb and H. Gilman, *J. Organomet. Chem.*, **20**, 281 (1969).
(8) A. E. Jukes, *Adv. Organomet. Chem.*, **12**, 272 (1974).
(9) K. M. Smirnov, A. P. Tomilov, and A. I. Shchekotikhin, *Russ. Chem. Rev.*, **36**, 326 (1967).
(10) M. R. Wiles and A. G. Massey. *Chem. Ind. (London)*, 663 (1967); *Tetrahedron Lett.*, 5137 (1967).
(11) M. D. Rausch, A. Siegel, and L. P. Klemann, *J. Org. Chem.*, **34**, 468 (1969).
(12) J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, *J. Chem. Soc., Perkin Trans. 1*, 763 (1972).
(13) M. R. Wiles and A. G. Massey, *J. Organomet. Chem.*, **47**, 423 (1973).
(14) W. Hübel in "Organic Synthesis Via Metal Carbonyls", Vol. I, I. Wender and P. Pino, Ed., Interscience, New York, N.Y., 1968, p 343.
(15) W. Hübel and C. Hoogzand, *Chem. Ber.*, **93**, 103 (1960).
(16) M. D. Rausch and R. A. Genetti, *J. Org. Chem.*, **35**, 3888 (1970).
(17) G. B. Kaufman and R. P. Pinell, *Inorg. Synth.*, **6**, 3 (1960).
(18) W. Hieber, E. O. Fischer, and E. Böckly, *Z. Anorg. Allg. Chem.*, **269**, 308 (1952).
(19) R. B. King, "Organometallic Syntheses", Vol. I, Academic Press, New York, N.Y., 1965, p 101.
(20) A shorter reflux period may be used, although **1** is obtained in somewhat lower yield.
(21) The preparations of pentafluorophenylcopper and phenyliodoacetylene were timed to coincide as closely as possible in order to minimize the formation of undesirable coupling products.

Preparation of 9-(5-Deoxy-α-D-arabinofuranosyl)adenine from D-Ribose[1]

Leon M. Lerner

Department of Biochemistry, State University of New York, Downstate Medical Center, Brooklyn, New York 11203

Aldofuranose derivatives that have three contiguous hydroxyl groups, with the hydroxyls at C-2 and C-3 in a cis relationship, will undergo epimerization at C-2 when acetolyzed in a mixture containing acetic acid, acetic anhydride, and sulfuric acid. This reaction was originally discovered by Jerkeman[2] and later studied in greater detail by Sowa[3] and others.[4] In recent years, it has been developed into a useful preparative reaction with hexofuranose derivatives, and optimal conditions have been found to consist of 10:1 acetic acid–acetic anhydride and 3–5% concentrated sulfuric acid.[5] This reaction has been useful in the development of new routes to rare sugars and in the synthesis of novel hexofuranosyl nucleosides.[6] Usually, no significant amounts of the reactant sugars or of their nucleosides have been found upon isolation of products. In more recent, unpublished experiments, it was found that certain 6-deoxyhexofuranosyl derivatives afforded only about a 50% yield of the C-2 epimerized products upon acetolysis. There was an interesting structural property of these latter derivatives that was striking. All of the original group of hexofuranose derivatives had hydroxyl groups at C-2 and C-3 which were on the same side of the furanose ring as the C-4 tail end of the sugar. In the cases involving incomplete epimerization the hydroxyl groups were on the opposite side of the ring from the C-4 group. It was of some interest, therefore, to compare results with a pentose having the same structural relationship. Because of the continuing interest in nucleosides of potential biological value, the preparation of 9-(5-deoxy-α-D-arabinofuranosyl)adenine (**5**) was undertaken starting from D-ribose.

D-Ribose was converted to methyl 2,3-O-isopropylidene-5-O-p-toluenesulfonyl-β-D-ribofuranoside (**1**) in two steps (Scheme I).[7] The terminal carbon atom was reduced with sodium borohydride in dimethyl sulfoxide[8] to afford methyl 5-deoxy-2,3-O-isopropylidene-β-D-ribofuranoside (**2**). Acetolysis of **2** gave a syrup (**3**) which was coupled with 6-benzamidochloromercuripurine in refluxing 1,2-dichloroethane in the presence of titanium tetrachloride.[9] The blocked nucleoside (**4**) was treated with sodium methoxide in methanol and **5** was obtained after purification by chromatography on an anion-exchange column.[10]

The elemental analysis of **5** indicated a nucleoside with the correct empirical formula. The UV spectrum supported a sugar linked to adenine at N-9. The melting point and optical rotation data are clearly different from either 9-(5-deoxy-β-D-ribofuranosyl)adenine[11] or 9-(5-deoxy-β-D-xylofuranosyl)adenine.[12] The slow rate of periodate consumption (0.87 molar equiv in 48 h) provided proof that the hydroxyl groups at C-2 and C-3 were arranged trans to each other, and this again eliminated the ribo configuration and, in addition, the lyxo configuration for the nucleoside. The data suggested that the product was **5**, which was what was expected from recent experience with this reaction pathway.[5,6]

The configuration of **5** at the anomeric carbon could not be deduced from the NMR spectrum because a trans arrangement for the H-1', H-2' protons can only be unequivocally concluded if $J_{1',2'} < 1$ Hz.[13] In this case, **5** had $J_{1',2'} = 4$ Hz. A comparison of the optical rotation of **5** with that of other pentofuranosyladenine nucleosides supported an α-D configuration. A proof of configuration was obtained by periodate