(10) We wish to thank Dr. R. C. Gueldner of the Boll Weevil Research Laboratory, USDA, Mississippi State, Miss. 39762, for comparing our samples with authentic samples.

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(12) NMR assignment of compound **7** was based on deuterium exchange study.

Synthesis of 4-Cyano-4'-halobiphenyls

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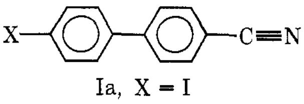
Received October 28, 1975

As part of a study of intermolecular halogen–cyanide interactions in the solid state it was desired to prepare very pure samples of the 4-cyano-4'-halobiphenyls. Pummerer and Seligsberger[1] have previously reported the synthesis of Ia and Niwa[2] has reported the synthesis of Ib and Ic. We wish to report the synthesis of these compounds by a different and very simple route involving the displacement of halogen with CuCN in refluxing dimethylformamide[3] (for the iodide and bromide) and N-methylpyrrolidone[4] (for the chloride).



Ia, X = I
b, X = Br
c, X = Cl

For the synthesis of Ia and Ib the reaction was run with 1 equiv of CuCN per mole of the dihalogenated biphenyl. The reaction mixture was very conveniently separated by preparative thin layer chromatography. In a few runs the main components of the reaction mixture were isolated and were approximately those expected for a statistical reaction. An attempt was made to run the displacement reaction on 4,4'-dichlorobiphenyl in refluxing dimethylformamide but even at long reaction times no product could be detected. Use of the higher boiling solvent N-methylpyrrolidone, an excess of CuCN, and long reflux times were necessary for a successful synthesis of Ic.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Laser Raman spectra were obtained with a Jeol Model JRS-S1 spectrometer equipped with an argon ion laser. Preparative thin layer chromatography was done on silica gel G PF-254 (E. Merck) using benzene as developer. Compounds were detected using an ultraviolet lamp and products extracted with methanol–chloroform (1:19). Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

4-Cyano-4'-iodobiphenyl (Ia). 4,4'-Diiodobiphenyl (0.50 g, 1.2 mmol), cuprous cyanide (0.11 g, 1.2 mmol), and 15 ml of dimethylformamide were placed in a 50-ml round-bottomed flask and refluxed for 2.5 hr. After cooling, 35 ml of ferric chloride solution (200 g of hydrated $FeCl_3$ and 50 ml of concentrated HCl in 300 ml of water) was added to the reaction vessel. The resulting mixture was heated at 60–70 °C for 20 min. The dimethylformamide–ferric chloride mixture was extracted three times with approximately 20 ml of toluene. The reddish toluene layer was then extracted with 50 ml of 10% HCl, 20 ml of water, and 50 ml of 5% NaOH. The toluene layer was dried over $MgSO_4$ and filtered. The toluene was evaporated at reduced pressure and the residue fractionated by preparative thin layer chromatography. The desired product has R_f 0.51 in benzene. The crude product was sublimed at 135 °C (1 mm), affording 4-cyano-4'-iodobiphenyl (160 mg, 42%). An analytical sample recrystallized from absolute ethanol melted at 179.5–181.5 °C (lit.[1] 166 °C), laser Raman (crystal) 2225 cm^{-1} (–C≡N).

Anal. Calcd for $C_{13}H_8NI$: C, 51.17; H, 2.64; N, 4.59; I, 41.59. Found: C, 51.05; H, 2.59; N, 4.58; I, 41.65.

4-Bromo-4'-cyanobiphenyl (Ib). The procedure was identical with one used for the iodo compound, except that 4,4'-dibromobiphenyl (0.50 g, 1.6 mmol) and cuprous cyanide (0.14 g, 1.6 mmol) were refluxed in dimethylformamide for 4.0 h. The R_f of 4-bromo-4'-cyanobiphenyl is 0.50 in benzene. The crude product was sublimed at approximately 120 °C (1 mm), producing 4-bromo-4'-cyanobiphenyl (210 mg, 50%). A sample recrystallized from absolute ethanol had mp 153.5–155 °C (lit.[2] 144 °C), laser Raman (crystal) 2225 cm^{-1} (–C≡N). An analysis of this compound was not performed. Its identity has been confirmed unambiguously by a complete x-ray analysis.[5]

4-Chloro-4'-cyanobiphenyl (Ic). The procedure used was similar to the one used for the iodo compound, except that 4,4'-dichlorobiphenyl (0.50 g, 2.2 mmol) and cuprous cyanide (0.40 g, 4.46 mmol) were refluxed for 93.0 h in N-methylpyrrolidone. The R_f of the product is 0.48 in benzene. The crude product was sublimed at about 105 °C (1 mm), affording 4-chloro-4'-cyanobiphenyl (110 mg, 23%). An analytical sample recrystallized from absolute ethanol melted at 133–133.5 °C (lit.[2] 129–130°C), laser Raman (crystal) 2225 cm^{-1} (–C≡N).

Anal. Calcd for $C_{13}H_8NCl$: C, 73.07; H, 3.77; N, 6.56; Cl, 16.60. Found: C, 73.24; H, 3.78; N, 6.45; Cl, 16.40.

Acknowledgment. We thank Professor Stuart Fenton for the laser Raman spectra and Professor Doyle Britton for his continued interest in this work.

Registry No.—Ia, 57774-34-2; Ib, 57774-35-3; Ic, 57774-36-4; cuprous cyanide, 544-92-3; 4,4'-diiodobiphenyl, 3001-15-8; ; 4,4'-dibromobiphenyl, 92-86-4; 4,4'-dichlorobiphenyl, 2050-68-2.

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A Convenient Synthesis of Labile Optically Active Secondary Alkyl Bromides from Chiral Alcohols

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Received September 25, 1975

Recent interest and reports[1-3] concerning the synthesis of optically active secondary alkyl halides prompts this disclosure of our experience in the area and of a convenient preparative procedure for active bromides, including those which are prone toward racemization.

Conceivably, one of the simplest approaches to the preparation of active halides involves treatment of the corresponding chiral alcohol with a phosphorus trihalide as in eq 1–4. Unfortunately, in practice this method has met with considerable difficulty primarily because the reactions represented by eq 3 and 4 are slow and have afforded halides of much lower optical purity.[1,4-6] To alleviate this problem, HX is commonly swept out (CO_2 or N_2) which essentially eliminates the last two steps (eq 3 and 4).

This produces product of high optical purity but the resulting low yields (i.e., 23% 2-bromooctane from 2-octanol)[1,7] severely limit the usefulness of the procedure, espe-