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(DICYANOIODO)BENZENE - A STABLE TRICOORDINATE IODINE(III) COMPOUND WITH THREE CARBON LIGANDS

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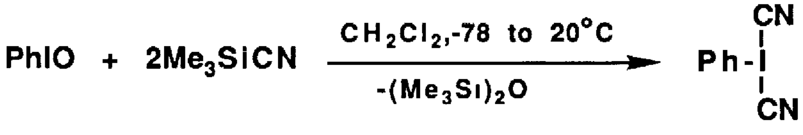
Summary *(Dicyanoiodo)benzene, a stable iodine(III) compound bearing three carbon ligands, was prepared by the reaction of PhIO with* Me_3SiCN

In recent years a large variety of polyvalent iodine compounds have become available, and their versatility in organic synthesis has been well established[1] The vast majority of known stable iodine(III) derivatives are ionic compounds with one or two carbon ligands covalently attached to a positively charged iodonium atom To the best of our knowledge, only two iodinanes bearing three carbon ligands have been reported, both being unstable at room temperature[2] These are compounds with three aromatic substituents at iodine triphenyl iodine[2a] and 5-phenyl-5H-dibenziodole[2b] Intermediate formation of tricoordinated iodinanes with three carbon ligands was also proposed in C-C bond forming reactions of iodonium reagents, but none of these intermediates have been isolated or observed by spectral methods[1a]

In this paper we wish to report the preparation of a stable tricoordinated iodinane with three carbon ligands, namely (dicyanoiodo)benzene 1 This compound was prepared in 50-70% yield by the reaction of iodosobenzene with trimethylsilyl cyanide[3] in methylene chloride as an air-sensitive crystalline solid, stable at room temperature under nitrogen for several weeks



$$PhIO + 2Me_3SiCN \xrightarrow[-(Me_3Si)_2O]{CH_2Cl_2,-78\ to\ 20°C} Ph\text{-}I(CN)_2$$

(1)

Typical procedure Trimethylsilyl cyanide (1 1 ml, 8 3 mmoles) was added to a stirred mixture of PhIO (0 9 g, 4 1 mmole) in 20 ml of CH_2Cl_2 at -78°C under nitrogen The mixture was allowed to warm to room temperature and was stirred an additional 30 min until formation of a clear solution Hexane (30 ml) was added, and the white crystalline precipitate (0 58 g, 55%) filtered under nitrogen Analytically pure material may be obtained by recrystallization from CH_2Cl_2-hexane solution **Caution:** All operations with compound **1** must be conducted under nitrogen, *otherwise it may explode when exposed to air*

Compound **1** was characterized by IR, NMR, mass-spectra and microanalysis[4]. The infrared spectrum displayed the characteristic absorbtion signals of the the cyano group at 2144 and 2130 cm^{-1} The ^1H NMR had the typical 2 1 2 aromatic signals characteristic of the phenyl group and the ^{13}C NMR spectrum showed five signals for the four carbons of the aromatic ring and the cyano groups in the region 135-105 ppm In the mass-spectrum a weak molecular peak (256) as well as peaks corresponding to PhI, C_2N_2, and ICN fragments were found

Our attempts to prepare tricyanoiodine by the analogous reaction of ICl_3 or $I(OCOCF_3)_3$ with Me_3SiCN led to formation of cyanogen iodine ICN via loss of the *dicyane molecule from the intermediate* $I(CN)_3$

In conclusion, isolation of compound **1** supports the proposed possibility for tricoordinated iodine intermediates in C-C forming reactions[1a] This compound is a potential source of cyano radical and may find application as a cyanating reagent

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4.Compound **1** mp 78-79 °C (dec), IR (in CCl_4) 3057, 2144, 2130, 1491, 1443, 985 cm^{-1}, ^1H NMR (CD_2Cl_2, δ) 8 24 (d, 2H), 7 75 (m, 1H), 7 63 (t, 2H), ^{13}C NMR (CD_2Cl_2, δ) *134 23, 133 24, 132 85,* 124 75 (CN), 106 77, MS (EI, 17 eV) $[M]^+$ 256 (9), $[C_6H_5I]^+$ 204 (100), $[ICN]^+$ 153 (9), $[C_6H_5]^+$ 77 (100), $[C_2N_2]^+$ 52 (3) Found, % C 37 09, H 2 12 Calc for $C_8H_5IN_2$ C 37 50, H 1 95

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