J. Org. Chem. 1989, 54, 2609-2612

Iodosobenzene Tetrafluoroborate, Hexafluoroantimonate, and Hexafluorophosphate: Stable Electrophilic Hypervalent Iodine Reagents without Nucleophilic Ligands

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Received October 14, 1988

Three novel iodine(III) derivatives—tetrafluoroborate (1), hexafluoroantimonate (2), and hexafluorophosphate (3)—were prepared by the reaction of (diacetoxyiodo)benzene with aqueous solutions of the corresponding acids. Reactions of these reagents with alkenes (cyclohexene, indene) in the presence of external nucleophiles (methanol, acetic acid, lithium perchlorate) yielded products of vicinal disubstitution. Silyl enol ethers reacted with reagents 1 and 3 to give products of oxidative coupling with high yield. Several alkynyliodonium salts were prepared from 1-pentyne and these reagents.

In its more than 100 years of history, hypervalent iodine chemistry has gone through many phases.[1] In recent years there has been a substantial increase in the level of interest in derivatives of iodine(III).[1a–e] Many of the new discoveries in this area have been connected with the preparation of novel types of I(III) reagents with the general formula R–I(X)Y, where X and Y are non-carbon ligands. Until 1970, only few such reagents were known, aryliodoso dicarboxylates and dihalogenides.[1f] But in 1970, O. Neiland and B. Karele synthesized PhI(OH)OTs, an example of a I(III) reagent with a good leaving group as a ligand.[2] Later G. Koser demonstrated that this reagent exhibited high electrophilic properties[3] and reacted with ketones,[3a] alkenes,[3b,c] acetylenes,[3b,d] and trimethylsilyl derivatives.[3e,f] It was shown that this reagent is a convenient precursor for the preparation of various iodonium salts: aryl and heteroaryl,[3e,f] vinyl,[3b,d] and alkynyl.[3b,d,4]

Recently our group prepared several iodine(III) reagents containing in their structures very weak nucleophilic ligands—perchlorate,[5a–c] triflate,[5a–c] sulfate,[5a,d] and mesylate.[5a,e] These reagents are very reactive and easily convert alkenes into 1,2-disubstituted products.[5,6] Reactions of these reagents with bridged bicyclic alkenes, such as norbornene, norbornadiene, and tricyclo[4.2.2.0^{2,5}]decane derivatives usually proceed with skeletal rearrangements due to their strong electrophilic properties.[5]

Another type of highly electrophilic I(III) reagent was discovered recently, complexes of PhIO with Lewis acids, such as BF_3/Et_2O and $Et_3O^+BF_4^-$.[7] These reagents can be used for oxidation of ketones and silyl enol ethers to α-hydroxy ketones,[7d] coupling of silyl enol ethers,[7e] allylation of aromatic compounds,[7h] functionalization of alkenes,[5a] allylsilanes,[7f] and β-dicarbonyl compounds[7g] in the presence of external nucleophiles, preparation of vinyl-[7b] and alkynyliodonium salts,[7c] and ring contraction in cycloalkenes.[8] The most important advantage of these complexes is the absence of nucleophilic ligands at the iodine atom and their highly electrophilic character. But both of these complexes are unstable and can be used only immediately after preparation at −10 to 0 °C. In this paper we report the synthesis and reactions of the first *stable* iodine(III) reagents with nonnucleophilic ligands: iodosobenzene tetrafluoroborate (1), hexafluoroantimonate (2), and hexafluorophosphate (3) (for preliminary communication dealing with the BF_4^- compound, see ref 4).

Results and Discussion

All three reagents were prepared by the same procedure: adding an aqueous solution of the corresponding acid to $PhI(OAc)_2$ in chloroform, vacuum evaporation at 40–50 °C, and crystallization of the final product by addition of a small amount of water. The same method was used before for preparation of iodosobenzene perchlorate and triflate.[5b] It is similar to Merkushev's procedure for the synthesis

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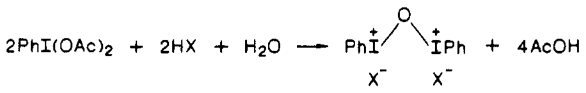
Table I. Reactions of Reagents 1-3 with Alkenes, Silyl Enol Ethers, and Acetylenes at 25 °C

unsaturated substrate	reagent	solvent (nucleophile)	time, h	product (yield, %)
indene	1	MeOH	1	**5** (30), **6** (60)
		AcOH	0.5	**7** (85)
	2	MeOH	0.5	**5** (35), **6** (57)
		AcOH	0.5	**7** (56)
	3	MeOH	1	**5** (21), **6** (59)
		AcOH	1	**7** (61)
cyclohexene	1	EtOAc ($LiClO_4$)	2	**8** (92)
	2	EtOAc ($LiClO_4$)	1	**8** (94)
	3	EtOAc ($LiClO_4$)	3	**8** (71)
10	1	CH_2Cl_2	1	**14** (94)
	3	CH_2Cl_2	2	**14** (90)
11	1	CH_2Cl_2	3	**15** (93)
	3	CH_2Cl_2	3	**15** (85)
12	1	CH_2Cl_2	1	**16** (89)
	3	CH_2Cl_2	1	**16** (78)
13	1	CH_2Cl_2	1	**17** (82)
1-pentyne	1	CH_2Cl_2	3	**18** (42)
	2	CH_2Cl_2	0.5	**19** (48)
	3	CH_2Cl_2	4	**20** (36)

of various aryliodoso dicarboxylates.[10] A general equation for the reaction is:

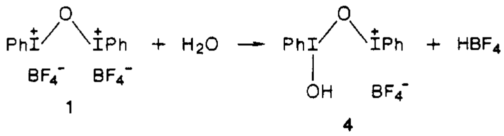


$$2PhI(OAc)_2 + 2HX + H_2O \longrightarrow Ph\overset{+}{I}\text{-}O\text{-}\overset{+}{I}Ph\ 2X^- + 4AcOH$$

1: X = BF_4
2: X = SbF_6
3: X = PF_6

Reagents **1**–**3** are yellow solids which are insoluble in water and nonpolar organic solvents (chloroform, methylene chloride, benzene, hexane) but soluble in dimethyl sulfoxide, acetonitrile, and methanol. Structures of compounds **1**–**3** were supported by data from ^{1}H, ^{13}C NMR, IR, and mass spectra. In the ^{1}H NMR spectra of all three reagents the only signals that appeared were from the monosubstituted phenyl ring with chemical shifts from 7.9 to 7.2 ppm. ^{13}C NMR spectra showed only three carbon signals with chemical shifts around 130 ppm. There were characteristic absorptions of C–I (460 cm^{-1}) and O–I (530 cm^{-1}) bonds in the IR spectra. Mass spectra with negative ion chemical ionization showed, for compound **2**, peaks 877 $[M - F]^-$ and 663 $[M - SbF_6]^-$, and for compounds **1** and **3**, fragments with lower molecular weights.

Compounds **1**–**3** are slightly hydrolyzed with water. When the tetrafluoroborate reagent **1** was worked up with large amounts of water for a long time (2–3 h) it gave the hydroxy derivative **4**, the structure of which was supported by spectral data and elemental analysis. It had a higher decomposition point (160 °C) than starting reagent **1** (120 °C) and was not as bright yellow in color, which is related to PhI^+OI^+Ph conjugation.[11]

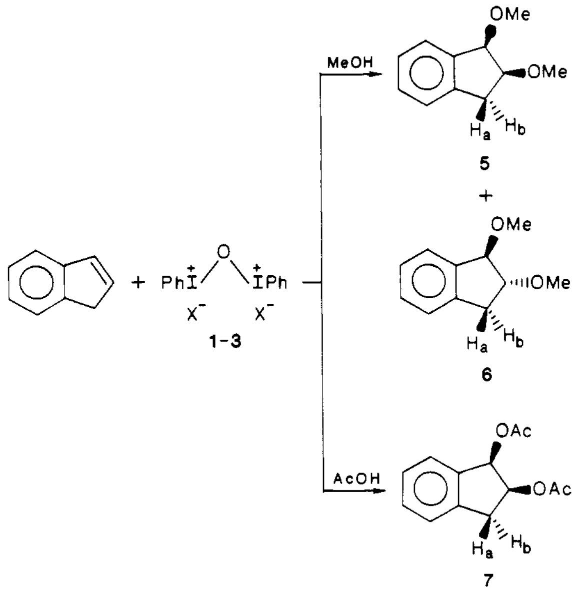


1 **4**

In fact, all three reagents **1**–**3** usually are contaminated with small impurities of hydrolyzed products, and their decomposition points, depending on amount of water used for washing, may vary from 100 to 160 °C. Presence of some contamination with hydrolyzed products was indicated also by an absorption band at about 3300 cm^{-1} in the IR spectra of compounds **1**–**3**. All three compounds **1**–**3** can be stored for several months in a refrigerator without any signs of decomposition, but solutions in DMSO, CH_3CN, or MeOH are unstable and completely lose their yellow color in 2–3 h. All three reagents are decolorized immediately with acetone, and compound **2** even reacts with ether.

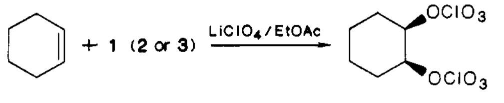
We have studied reactions of reagents **1**–**3** with alkenes, silyl enol ethers, and alkynes. The reaction conditions and yields of the products are listed in Table I.

All three reagents reacted immediately with indene in MeOH or AcOH to give products of vicinal disubstitution:



The product yields in these reactions essentially did not depend on the nature of the starting reagent. Reactions in methanol yielded mixtures of cis and trans isomers, the structures of which were determined by ^{1}H NMR spectra. Configurational assignments of the methoxy groups were determined on the basis of chemical shifts of protons in the CH_2 group. There was a big difference (0.52 ppm) in the $\Delta\delta$ of these protons in the cis isomer **5** due to the deshielding effect of the two neighboring *cis*-methoxy groups on H_a, and no difference in the chemical shifts of H_a and H_b for the trans isomer **6**. Reactions of indene in acetic acid gave only one product, the *cis*-diacetate **7**. The ^{1}H NMR spectrum of this compound showed a big difference between the chemical shifts of H_a and H_b (0.63 ppm), consistent with a cis configuration for the acetoxy groups.

Reactions of reagents **1**–**3** with cyclohexene in AcOH or MeOH led to complex mixtures of products. Reactions in ethyl acetate in the presence of lithium perchlorate as an external nucleophile, however, yielded only one major product, the *cis*-diperchlorate **8**.



8

This product (**8**) was identical in its spectral and chromatographic characteristics with a sample synthesized from iodosobenzene perchlorate and cyclohexene.[5b]

The difference in stereochemistry of reactions in MeOH from those in AcOH or $LiClO_4$/EtOAc possibly can be explained by changes in mechanism due to different degrees of neighboring group participation in the interme-

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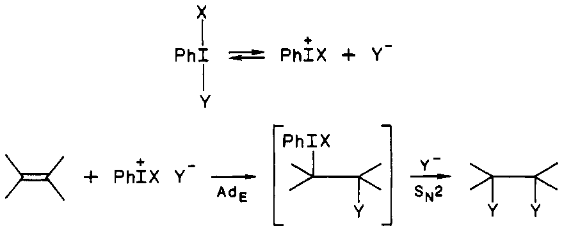
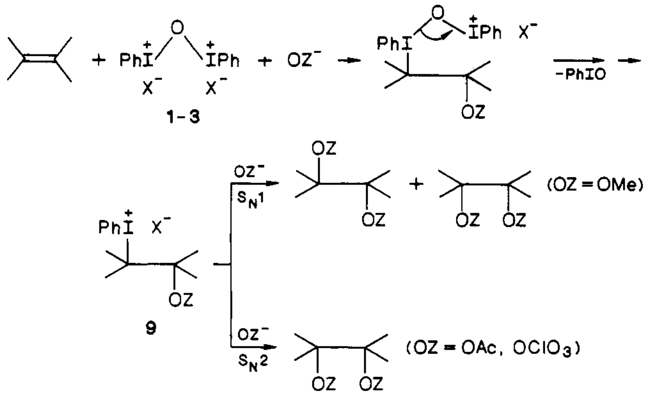
diates of these reactions although the change in solvent systems might also influence the stereochemical course of the reaction. A two-step mechanism is usually proposed for reactions of I(III) reagents with alkenes—electrophilic addition of ionized reagent in the first step and nucleophilic substitution of the PhI moiety in the second step.[3b,c,5]

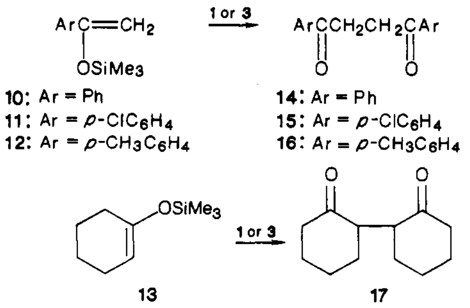


In the case of a strong electron-withdrawing group Y, such as OTs, $OClO_3$, OTf, and even OAc, the second step proceeds as a S_N2 substitution to give only the cis product.[3b,c,5] But if Y is an electron-donating group that stabilizes the carbocationic intermediate, it can change the mechanism to S_N1, and as a result, the reaction loses its stereoselectivity. It is very likely that this is the reason for the nonstereoselectivity of the reactions of reagents **1–3** with indene in methanol. The first step proceeds as an electrophilic trans addition with involvement of external nucleophile OZ^- to give intermediate **9** with OZ = OMe:



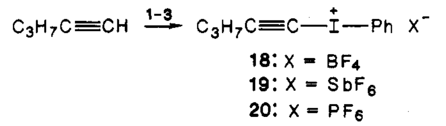
The second step proceeds as a S_N1 substitution (due to stabilization of the carbocationic intermediate by the methoxy group), yielding mixtures of cis and trans isomers. In the cases of acetic acid and $LiClO_4$ as external nucleophiles, the second step gives only the cis product as the result of the usual S_N2 substitution.

We have studied oxidative couplings of silyl enol ethers **10–13** with reagents **1–3**. We found that these reagents (with one exception) react fast with silyl enols to give substituted 1,4-butanediones **14–17** as major products. The only exception was reagent **2**, which reacted with silyl enol ethers almost immediately to give a dark tar.



Products of the reactions with reagents **1** or **3** were identified by comparison of their spectral data and physical characteristics with those previously reported.[7e,12] It is worth emphasizing that the previously reported attempt at coupling of the silyl enol ether of cyclohexanone with the electrophilic complex $PhIO/BF_3$ was unsuccessful.[7e] We explain the formation of products **14–17** with the same mechanism as proposed by Moriarty for couplings of silyl enol ethers with $PhIO/BF_3$.[7e]

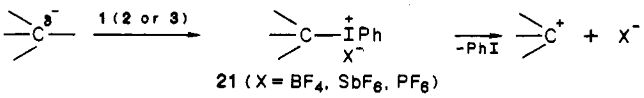
Reactions of reagents **1–3** with 1-pentyne yielded alkynyliodonium salts **18–20**, whose spectral characteristics were similar to data reported by M. Ochiai et al for alkynyl tetrafluoroborates.[7c] Products **18–20** were unstable, and decomposed in a few hours to give a black tar.



$$C_3H_7C{\equiv}CH \xrightarrow{1-3} C_3H_7C{\equiv}C{-}\overset{+}{I}{-}Ph\ X^-$$

18: X = BF_4
19: X = SbF_6
20: X = PF_6

All of the reactions reported in this paper show the high electrophilic properties of reagents **1–3**, comparable with the reactivity of $PhIO/BF_3$. This reactivity can be increased further by the addition of catalytic amounts of HBF_4/Me_2O into the reaction mixture. The principal differences between reagents **1–3** and the complex of PhIO with BF_3/Et_2O are (i) their enhanced stability and (ii) in contrast to $PhIO/BF_3$, reagents **1–3** can give in their reactions with silyl enol ethers and other C-nucleophiles relatively stable iodonium salts **21** with stable nonnucleophilic anions (BF_4^-, SbF_6^-, PF_6^-) according to the general scheme:



21 (X = BF_4, SbF_6, PF_6)

Iodonium salts **21**, which contain in their structures one of the best leaving groups, PhI, can find application in organic synthesis as synthetic equivalents of carbocations.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on an IBM AF FT NMR spectrometer (200 MHz) with tetramethylsilane as the internal reference. Mass spectra were obtained with a Hewlett-Packard 5970 A GC mass spectrometer and a Finnigan MAT 4500 quadrupole mass spectrometer.

Iodosobenzene diacetate, hydrogen tetrafluoroborate, hexafluoroantimonate, and hexafluorophosphate, indene, cyclohexene, lithium perchlorate, 1-pentyne, silyl enol ethers of acetophenone, and cyclohexanone were obtained commercially. Silyl enol ethers of *p*-methyl- and *p*-chloroacetophenones were prepared by known procedures.[7e]

General Procedure for Preparation of Reagents 1–3. To a stirred solution of 3.22 g (10 mmol) of iodosobenzene diacetate in 5 mL of chloroform was added 11–12 mmol of the corresponding acid (2 mL of 48% HBF_4, 4 g of 65% $HSbF_6$ or 2.5 mL of 65% HPF_6 water solutions) at room temperature. The resulting solution was evaporated in vacuum for 30 min at 50 °C to give a yellow oil, which was crystallized by addition of 10 mL of chloroform and 2 mL of water. The yellow crystals were filtered, washed with chloroform (30 mL) and water (30 mL), and dried in a dessicator over phosphorus pentoxide in vacuum.

Iodosobenzene tetrafluoroborate (1): yield 2.1 g (70%); mp 130–140 °C dec; ^1H NMR (20% DMSO-d_6 in $CDCl_3$) δ 7.8 (2 H, d, J = 7.6 Hz), 7.6 (1 H, t, J = 7.2 Hz), 7.5 (2 H, t, J = 7.5 Hz); ^{13}C NMR (20% DMSO-d_6 in $CDCl_3$) δ 133.4, 131.5, 130.7; IR (KBr, cm^{-1}) 3060, 1575 (Ph), 1150–1000 (BF_4^-), 530 (I–O), 460 (I–C).

Iodosobenzene hexafluoroantimonate (2): yield 3 g (67%); mp 110–120 °C dec; ^1H NMR (20% DMSO-d_6 in $CDCl_3$) δ 7.7 (2 H, d, J = 7.5 Hz), 7.4 (1 H, t, J = 7.0 Hz), 7.3 (2 H, t, J = 7.6 Hz); ^{13}C NMR (20% DMSO-d_6 in $CDCl_3$) δ 133.0, 131.4, 130.4; IR (KBr, cm^{-1}) 3070, 1585 (Ph), 550 (I–O), 425 (I–C); MS (negative

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chemical ionization, argon, 30 eV) m/e 663 $[M - SbF_6]^-$, 877 $[M - F]^-$.

Iodosobenzene hexafluorophosphate (3): yield 2.0 g (65%); mp 115–120 °C dec; ^1H NMR (20% DMSO-d_6 in $CDCl_3$) δ 7.7 (2 H, d, J = 7.5 Hz), 7.4 (1 H, t, J = 7.2 Hz), 7.3 (2 H, t, J = 7.4 Hz); ^{13}C NMR (20% DMSO-d_6 in $CDCl_3$) δ 132.8, 131.1, 130.3; IR (KBr, cm^{-1}) 3080, 1585 (Ph), 550 (I–O), 430 (I–C).

Hydrolysis of Iodosobenzene Tetrafluoroborate (1). A mixture of reagent 1 (0.3 g, 0.5 mmol) with water (500 mL) was stirred for 2 h. Pale yellow crystals of product were filtered, washed additionally with 500 mL of water, and dried in a vacuum dessicator over phosphorus pentoxide to give 0.25 g (95%) of the hydroxy derivative 4: mp 150–160 °C dec; ^1H NMR (DMSO) δ 7.8 (2 H, d, J = 7.8 Hz), 7.7 (2 H, d, J = 7.2 Hz), 7.6 (1 H, t, J = 7.1 Hz), 7.5 (1 H, t, J = 7.4 Hz), 7.45 (2 H, t, J = 7.3 Hz), 7.2 (2 H, t, J = 7.5 Hz), 3.39 (1 H, s); ^{13}C NMR (DMSO) δ 136.9, 133.4, 131.5, 131.4, 130.6, 128.5; IR (Nujol, cm^{-1}) 3420, 3060, 1575, 530, 460. Anal. Calcd for $C_{12}H_{11}BF_4I_2O_2$: C, 27.30; H, 2.10. Found: C, 27.70; H, 1.99.

Reactions of Reagents 1–3 with Indene. Reagent (**1**, **2**, or **3**) (0.5 mmol) was added to a stirred solution of indene (0.12 g, 1 mmol) in 3 mL of methanol or acetic acid at room temperature. The reaction mixture was stirred at room temperature until its color completely disappeared, diluted with 15 mL of water, and extracted with CH_2Cl_2. The organic solution was dried with Na_2SO_4, the solvent was evaporated, and the products were separated by column chromatography (silica gel, ethyl acetate–hexane, 1:2).

***cis*-1,2-Dimethoxyindan (5)**: ^1H NMR ($CDCl_3$) δ 7.30 (4 H, m), 4.74 (1 H, d, J = 4.2 Hz), 4.10 (1 H, m), 3.57 (3 H, s), 3.47 (3 H, s), 3.32 (1 H, dd, J = 16.0 and 6.9 Hz), 2.80 (1 H, dd, J = 16.0 and 5.4 Hz); MS m/z 178 (M^+).

***trans*-1,2-Dimethoxyindan (6)**: ^1H NMR ($CDCl_3$) δ 7.38 (4 H, m), 4.61 (1 H, d, J = 4.9 Hz), 4.08 (1 H, td, J = 7.2 and 4.9 Hz), 3.51 (3 H, s), 3.42 (3 H, s), 3.90 (2 H, dd, J = 7.2 and 2.8 Hz); MS m/z 178 (M^+).

***cis*-1,2-Diacetoxyindan (7)**: ^1H NMR ($CDCl_3$) δ 7.30 (4 H, m), 6.26 (1 H, d, J = 3.6 Hz), 5.49 (1 H, ddd, J = 7.1, 4.5, and 3.5 Hz), 3.53 (1 H, dd, J = 16.7 and 7.1 Hz), 2.90 (1 H, dd, J = 16.7 and 4.5 Hz), 2.10 (3 H, s), 2.08 (3 H, s); MS m/z 174 ($M^+ - AcOH$).

Reactions of Reagents 1–3 with Cyclohexene in the Presence of $LiClO_4$. A mixture of the reagent (**1**, **2**, or **3**) (0.05 mmol), cyclohexene (0.2 mL), lithium perchlorate (0.5 g), and ethyl acetate (3 mL) was stirred until its color completely disappeared, diluted with CH_2Cl_2, washed with water, and dried. The solvent was removed by evaporation. Iodobenzene and diperchlorate 8 were separated by column chromatography (silica gel, ethyl acetate–hexane, 1:5). For 1,2-bis(perchloryloxy)cyclohexane 8:[4b] ^1H NMR ($CDCl_3$) δ 5.17 (2 H, m, W = 12 Hz), 2.0–1.5 (8 H, m). **Caution**: neat diperchlorate 8 can explode violently on contact or heating.

Reactions of Reagents 1 and 3 with Silyl Enol Ethers. A mixture of reagent (**1** or **3**) (0.05 mmol), silyl enol ether (0.2 mmol), and CH_2Cl_2 (2 mL) was stirred at room temperature until the reagent completely disappeared. The reaction mixture was washed with water and dried with Na_2SO_4, and the solvent was evaporated. Crystals of 1,4-butanedione that formed were washed with hexane to remove iodobenzene and dried. Physical characteristics and spectral data for products **14–16**[7e] and **17**[12] were the same as previously reported.

Reactions of Reagents 1–3 with 1-Pentyne. A mixture of reagent (**1**, **2**, or **3**) (0.05 mmol) and 0.2 mL of 1-pentyne in 3 mL of CH_2Cl_2 was stirred at room temperature until the reagent completely disappeared. The solution was dried with Na_2SO_4, and the solvent was evaporated. Washing of the crude product with hexane to remove excess alkyne gave the alkynyliodonium salts **18–20** as unstable oils.

1-Pentynylphenyliodonium tetrafluoroborate (18): ^1H NMR ($CDCl_3$) δ 8.01 (2 H, m), 7.61 (3 H, m), 2.58 (2 H, t, J = 7.1 Hz), 1.59 (2 H, m), 0.94 (3 H, t, J = 7.3 Hz); IR (Nujol, cm^{-1}) 2200 ($C\equiv C$).

1-Pentynylphenyliodonium hexafluoroantimonate (19): ^1H NMR ($CDCl_3$) δ 8.05 (2 H, m), 7.71 (1 H, m), 7.58 (2 H, m), 2.63 (2 H, t, J = 7.1 Hz), 1.62 (2 H, m), 0.95 (3 H, t, J = 7.2 Hz); IR (Nujol, cm^{-1}) 2190 ($C\equiv C$).

1-Pentynylphenyliodonium hexafluorophosphate (20): ^1H NMR ($CDCl_3$) δ 8.04 (2 H, m), 7.51 (3 H, m), 2.52 (2 H, t, J = 6.8 Hz), 1.61 (2 H, m), 0.94 (3 H, t, J = 7.0 Hz); IR (Nujol, cm^{-1}) 2200 ($C\equiv C$).

Acknowledgment. We wish to thank the IREX exchange program for sponsoring V. V. Zhdankin's visit to the University of Minnesota, Duluth. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Iptycene Synthesis. A New Method for Attaching a 2,3-Anthracene Moiety to the 9,10-Positions of Another Anthracene Moiety. Exceptional Conditions for a Lewis Acid Catalyzed Diels–Alder Reaction[1]

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Received November 22, 1988

An efficient three-step method for appending a 2,3-anthracene moiety to the 9,10-positions of an existing anthracene moiety is described. The first step uses excess 1,4-anthraquinone (3 equiv) and aluminum chloride (6 equiv) to obtain the anthracene–quinone cycloadduct (omission of the $AlCl_3$ resulted in no adduct). The resulting diketone was reduced to the corresponding diol (excess $LiAlH_4$), which was dehydrated to the arene with phosphorus oxychloride and pyridine. Specific examples include the preparation of heptipycene **8** from pentiptycene **6** (66% overall yield) and a similar conversion of **8** to the noniptycene **13** (75% overall yield). The methodology led to a markedly improved synthesis of tritriptycene **9** and the first synthesis of undecaiptycene **14**.

Iptycenes have a rigid carbon framework, show exceptional thermal stability, and have well-defined molecular cavities that may trap small molecules.[2] The development of general methodology for their synthesis therefore constitutes a significant synthetic challenge.

One method for rapidly constructing higher iptycenes[2,3] involves attaching a 2,3-anthracene moiety to the 9,10-

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[1] Presented at the Midwest-America Chinese Science and Technology Conference, St. Louis, MO, June 4, 1988.

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0022-3263/89/1954-2612$01.50/0 © 1989 American Chemical Society