

Solid-Phase Iodination of Arenes with the System Iodine–Diacetoxy(phenyl)- λ^3 -iodane

E. A. Krasnokutskaya, M. E. Trusova, and V. D. Filimonov

Tomskii politekhnicheskii universitet State Higher Professional Education Enterprise, pr. Lenina 30, Tomsk, 634050 Russia
e-mail: e_krasnokutskaya@mail.ru

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Abstract—The system iodine–diacetoxy(phenyl)- λ^3 -iodane in the solid phase is capable of iodinating activated arenes.

Aromatic iodides are indispensable components in many chemical transformations. In addition, some iodinated arenes attract interest as important biologically active compounds, radiopaque materials, and radiopharmaceutical preparations [1]. Reactions occurring in the solid phase without a solvent constitute a promising line in modern organic synthesis. However, studies on electrophilic aromatic iodination under solvent-free conditions have been initiated only recently. The iodinating power in the solid phase of such reagents as Me_4NCl_2 [2], I_2 , ICl , and *N*-iodosuccin-

imide [3] was reported. An example of solid-phase oxidative electrophilic iodination with iodine and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was described in [4]. The solid-phase reaction of durene with HI adsorbed on silica gel in the presence of PhIO gave a mixture of the corresponding mono- and diiodo derivatives in a poor yield (17 and 12%, respectively) [5].

The goal of the present work was to elucidate some relations holding in solid-phase oxidative iodination with the system $\text{I}_2\text{--PhI}(\text{OAc})_2$ (**I**) at room temperature under mechanical activation; examples of the applica-

Iodination of arenes **II–VIII** with $\text{I}_2\text{--}(\text{AcO})_2\text{I}$ in solution and under solvent-free conditions at room temperature

Substrate/reagent	Solvent	Reaction time, h	Product (yield, %)	mp, °C
II/I	No solvent	0.75	4-Iodoanisole (33, strong tarring)	51–52 (50–53 [2])
II/I [6]	AcOEt	16	4-Iodoanisole (85)	
III/I	No solvent	0.75	Iododurene (80)	78–79
III/I $_2\text{--AcO}_2\text{H}$ [8] ^a	AcOH	1	Iododurene (86)	78
IV/I	No solvent	0.75	4,4'-Diiiododiphenyl ether (70)	139–140 (138–139 [12])
IV/I ^a [6]	AcOEt	16	4,4'-Diiiododiphenyl ether (70)	
V/I	No solvent	0.75	4-Iodobiphenyl (70)	112–113
V/I $_2\text{--AcO}_2\text{H}$ ^b [10]	AcOH	3.5	4-Iodobiphenyl (62)	109–111
V/I ^a [6]	AcOEt	16	4-Iodobiphenyl (12)	
VI/I	No solvent	0.75	4-Iodoacetanilide (75)	182–183 (184–186 [2])
VII/I	No solvent	0.75	2-Iodofluorene (70)	124–125
VII/I $_2\text{--AcO}_2\text{H}$ ^b [11]	AcOH	6	2-Iodofluorene (65)	126–127
VIII/I	No solvent	0.75	2,7-Diiiodofluorenone ^c (40)	205–206
VIII/I [9]	AcOH–Ac ₂ O–H ₂ SO ₄	0.25	2,7-Diiiodofluorenone (80)	203–204

^a At 60°C.

^b At 50°C.

^c The product was isolated by column chromatography using hexane–benzene (1 : 1) as eluent.

tion of that system to reactions in solution were reported in [6–11]. As substrates we used anisole (**II**), durene (**III**), diphenyl ether (**IV**), biphenyl (**V**), acetanilide (**VI**), fluorene (**VII**), and fluorenone (**VIII**), i.e., compounds for which liquid-phase iodination with system **I** was extensively studied.

Diacetoxy(phenyl)- λ^3 -iodane was found to oxidize iodine in the solid phase to produce reactive electrophilic species (acetyl hypoiodite AcOI was presumed to be the reactive species in solution [6–11]). Under solvent-free conditions, system **I** showed a moderate activity. It was capable of oxidizing activated arenes **II–VIII** but was inert with respect to deactivated *p*-nitrotoluene. The same reactivity is intrinsic to system **I** in solution [6–11]. In most cases, the yields of the isolated product were greater than in solution (see table), and the reactions were faster. An exception was anisole (**II**). The solid-phase iodination of this substrate was accompanied by strong tarring, and the yield of the iodination product was lower.

EXPERIMENTAL

Iodination of compounds II–VIII (general procedure). Elemental iodine was ground with an equimolar amount of diacetoxy(phenyl)- λ^3 -iodane over a period of 5 min. Arene **II–VIII**, 2 equiv, was added to the reagent thus prepared, and the mixture was quickly ground in an agate mortar; in all cases, the mixture melted. It was kept at room temperature for a time indicated in table and treated with a 15% solution of sodium sulfite, and the precipitate was filtered off and recrystallized from appropriate solvent. The products were identified by comparing their melting points and

spectral parameters (^1H and ^{13}C NMR) with those of authentic samples.

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