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Reactivity of Diacyloxyiodobenzenes Toward Trivalent Phosphorus Nucleophiles

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ABSTRACT: *The reaction of diacyloxyiodobenzenes and tetravalent phosphorus nucleophiles was investigated. It was established that both H-phosphonates and secondary phosphine oxides react with diacetoxyiodobenzene in alcohols in the presence of sodium alcoholates yielding trialkyl phosphates and alkyl phosphinates respectively. For this transformation reactive intermediate* **6** *is proposed. In contrast to this, the treatment of diacetoxyiodobenzene with 3 equiv of sodium diisopropyl phosphite in THF produces diisopropyl 1-(diisopropoxyphosphinyl)ethylphosphonate with excellent yield. It was found that diacyloxyiodobenzene/PR_3 system may serve as an acylating agent; the acylation process can proceed via carboxylic acid anhydride or acylphosphonium salt* **17** *depending on the protocol used. New very efficient method for synthesis of 2,4,6-trimethylbenzoic anhydride was developed.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:352–359, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10161

INTRODUCTION

[Bis(acyloxy)iodo]arenes are the most important, well investigated, and useful organic derivatives of iodine(III). Two of these, diacetoxyiodobenzene and [bis(trifluoroacetoxy)iodo]benzene, are commercially available or can be easily prepared by oxidation of iodobenzene with the respective peracid. In the last 20 years [bis(acyloxy)iodo]arenes have found widespread application as general, universal oxidizing reagents, and radical initiators [1]. Primary carboxamides undergo readily a Hofmann-type rearrangement with several iodanes, leading to amines or some of their derivatives. The reagent of choice for this rearrangement appears to be $PhI(OOCCH_3)_2$, as well as $PhI(OOCCF_3)_2$, both of which are used with a large variety of amides [2].

To the best of our knowledge polyvalent iodine compounds have not been explored extensively in the field of organophosphorus chemistry. As early as 1977, Foss et al. [3] presented the effectiveness of iodosylbenzene in the oxidation of the trivalent phosphorus organic compounds phosphines and diphosphines, which were transformed into phosphine oxides. For this transformation a phosphorus attack on the oxygen atom of iodosylbenzene was suggested. In 1979, the synthesis of [hydroxy-[(bis(phenyloxy)phosphoryl]oxy]iodobenzene in the reaction of diacetoxyiodobenzene with diphenyl phosphate in aqueous acetonitrile was published [4]. This compound generally has a reactivity pattern similar to [hydroxy(tosyloxy)iodo]benzene. It reacts with enolizable ketones affording the products of α-phosphoryloxylation [5].

Recently we investigated the reaction of iodosylbenzene with >P(O)H acids, which in aprotic solvents yields oxidation products, i.e. >P(O)OH acids and/or >P(O)OP(O)< anhydrides. If the reaction is performed in alcohol ROH as solvent in the presence of sodium alcoholate, a >P(O)OR ester is the major product [6].

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Because of our interest in the reactivity of phosphorus nucleophiles in halophilic substitution reactions [7,8], we also studied the reaction of >P(O)H acids and >P—O⁻ anions with diacetoxyiodobenzene. In these reactions oxidation of the starting compound is expected to give a major product. On the other hand, we recently demonstrated that in case of iodosylbenzene the oxidation depends on the constitution of phosphorus reagent as well as on the solvent used (especially in case of hydroxylic solvents) and the reaction course is not so obvious [6].

RESULTS AND DISCUSSION

Reaction of $R^1R^2P(O)H$ **1** *Acids with Diacetoxyiodobenzene* **2a**

In the first set of experiments, we treated diacetoxyiodobenzene **2a** with >P(O)H **1** acids (such as diisopropyl phosphite, phenylphosphinic acid isopropyl ester, di-*n*-hexylphosphine oxide, and *tert*-butylphenylphosphine oxide), in *i*-PrOH or MeOH as a solvent. The results are presented in Table 1.

As one can see (run 2) diisopropyl phosphite does not react with **2a** even after 24 h in boiling *i*-PrOH. In contrast to that, secondary phosphine oxides both in MeOH and in *i*-PrOH furnish phosphinic acids **4** and their esters **3**.

A second set of experiments was done in the presence of sodium alcoholate. From these reactions we isolated phosphates, phosphonates, or phosphinates **3** respectively, in moderate to almost quantitative yield. These results are also presented in Table 1 (see also Scheme 1).

TABLE 1 Reaction of $R^1R^2P(O)H$ Acids **1** with Diacetoxyiodobenzene **2a** in Alcohols

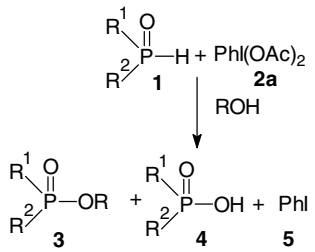
						Yield (%)	
Run	R^1	R^2	*R*	*Solvent*	*Alcoholate*	**3**	**4**
1[a]	*i*-PrO	*i*-PrO	Me	MeOH		38[b]	
2[a]	*i*-PrO	*i*-PrO	*i*-Pr	*i*-PrOH		0	0
3	*i*-PrO	*i*-PrO	*i*-Pr	*i*-PrOH	*i*-PrONa	100	
4	Ph	*i*-PrO	Me	MeOH		64	27
5	Ph	*i*-PrO	*i*-Pr	*i*-PrOH		60	20
6	Ph	*i*-PrO	*i*-Pr	*i*-PrOH	*i*-PrONa	85	10
7	*n*-C_6H_{12}	*n*-C_6H_{12}	Me	MeOH		49	40
8	*n*-C_6H_{12}	*n*-C_6H_{12}	Me	MeOH	MeONa	82	
9	*n*-C_6H_{12}	*n*-C_6H_{12}	*i*-Pr	*i*-PrOH		45	42
10	*n*-C_6H_{12}	*n*-C_6H_{12}	*i*-Pr	*i*-PrOH	*i*-PrONa	57	40
11	*t*-Bu	Ph	Me	MeOH		49	40
12	*t*-Bu	Ph	Me	MeOH	MeONa	90	
13[c]	*t*-Bu	Ph	*i*-Pr	*i*-PrOH		13[b]	34
14[d]	*t*-Bu	Ph	*i*-Pr	*i*-PrOH	*i*-PrONa	30[b]	45

[a]In this experiment starting material was observed by ^1H and ^{31}P NMR.
[b]Yields estimated by ^1H and ^{31}P NMR.
[c]*tert*-Butylphenylphosphinic acid anhydride with 35% of yield was isolated.
[d]*tert*-Butylphenylphosphinic acid anhydride with 16% of yield was isolated.

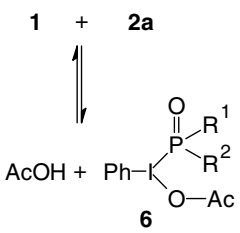
As one can see from the data presented in Table 1, **2a** in the reaction with >P(O)H acids **1** in alcohols produces >P(O)OR esters **3** and >P(O)OH acids **4** in comparable yields. In contrast to that in the presence of sodium alcoholates, esters **3** are formed in quantitative yield. This strongly suggest that ester **3** is derived from the initial halophilic substitution product **6**, which is an activated form of phosphoric (phosphinic) acid (see Scheme 2). The intermediate **6** may participate in two competiting processes a and b (Scheme 3). In pathway a, intermediate **6** breaks into iodobenzene and the mixed anhydride **7**, which in the reaction with alcohol will produce alkyl acetate and phosphoric/phosphinic acid **4**. On the other hand if there is an alcoholate anion acting as a strong nucleophile in the reaction mixture, it will react fast enough with intermediate **6** to produce ester **3** and iodobenzene **5** in high yield.

To provide evidence for our hypothesis, we monitored, by ^{31}P NMR spectroscopy, the reaction between diacetoxyiodobenzene and di-*n*-hexylphosphine oxide in $CDCl_3$ (see Fig. 1). The spectrum of the reaction mixture exhibits three resonance lines: $\delta^{31}P = 39.18$ ppm (di-*n*-hexylphosphine oxide **1**, $R^1{=}R^2{=}C_6H_{12}$), 60.23 ppm (*O*-acetyl di-*n*-hexylphosphinate **7**, $R^1{=}R^2{=}C_6H_{12}$, confirmed with an authentic sample), and 61.84 ppm (unknown phosphorus compound). When methanol was added to this reaction mixture, the unknown phosphorus compound was consumed, while methyl di-*n*-hexylphosphinate **3** ($\delta^{31}P = 63.55$ ppm) and di-*n*-hexylphosphinic acid **4** ($\delta^{31}P = 55.56$ ppm) were observed. These results confirm that **3** originated from the reaction of methanol with **7** but with the compound resonating at $\delta^{31}P = 61.84$ ppm, which we believe has structure **6** ($R^1{=}R^2{=}C_6H_{12}$), which is presented in Schemes 2 and 3.

As shown in runs 2 and 3, diisopropyl phosphite does not react with diacetoxyiodobenzene



SCHEME 1



SCHEME 2

in *i*-PrOH, but produces triisopropyl phosphate in quantitative yield in the presence of sodium isopropanolate. When we treated **2a** with sodium diisopropyl phosphite **8** in THF, to our surprise, from the reaction mixture besides **5** and recovered **2a**, we also isolated diisopropyl phosphate **4a** and diisopropyl 1-(diisopropylphosphinyl) ethylphosphonate **9** (Scheme 4).

Recovery of starting material **2a** from this reaction mixture strongly suggests that **8** is consumed in the same competition process in which compound **9** is produced. On the other hand it is well known [7–12] that compound **9** is a rearranged product of corresponding 1-hydroxyethylbisphosphonate **11**. Taking into consideration the isolation of **9** and **4a** from the reaction of **8** with **2a** in THF, one can conclude that in the reaction under investigation *O*-acetyl diisopropyl phosphate **7a** reacts with diisopropyl phosphite anion to yield diisopropyl α-ketophosphonate **10** (Scheme 5, Eq. (3)), which in the reaction with sodium diisopropyl phosphite will produce **11** (Scheme 5, Eq. (4)). To get a closer look of this transformation we carried out the reactions of 1 equiv of **2a** with different amounts of **8** under standard conditions (THF, 1 h, 20°C). The results of this set of experiments are presented in Table 2. As one can see, the product distribution strongly depends on the ratio **8/2a**. The yield of **9** and **4a** increases with the increase in concentration of **8** used, which is in full agreement with the stoichiometry presented in Scheme 5.

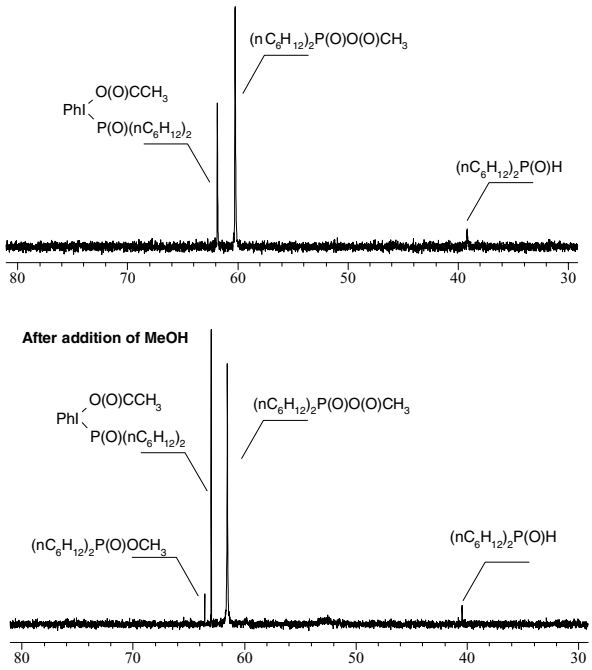
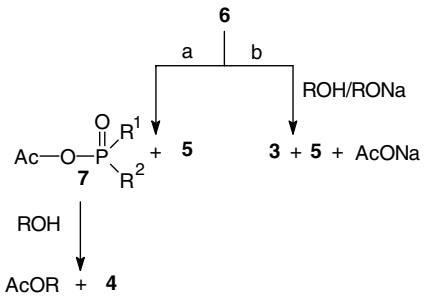
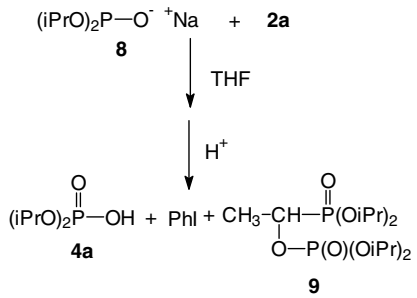


FIGURE 1 ^{31}P NMR spectrum of reaction mixture composed from diacetoxyiodobenzene and di-*n*-hexylphosphine oxide.

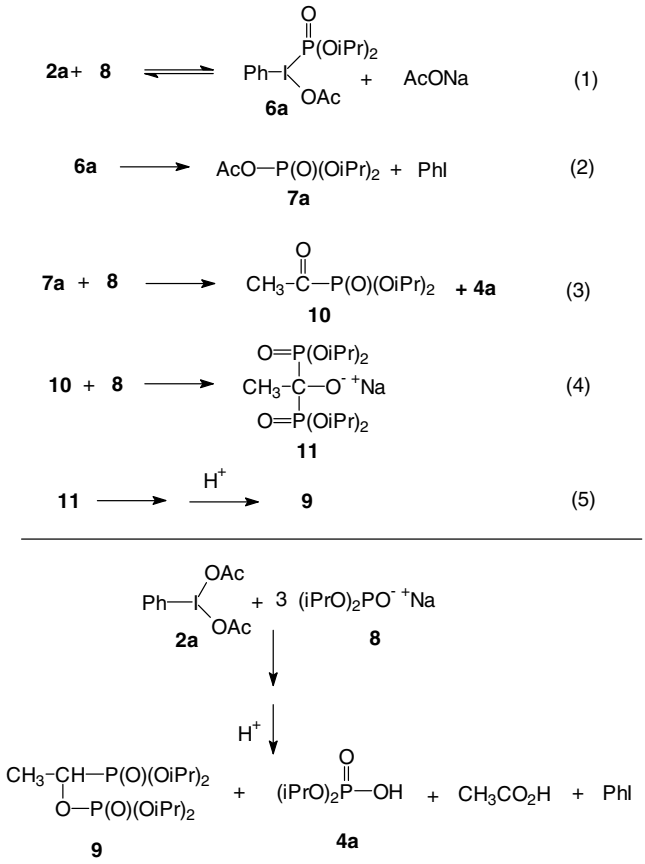
However, at this point one can also argue that the diisopropyl phosphite anion can attack carbonyl carbon atom in **2a** to produce the α-ketophosphonate **10** and iodosobenzene, which could oxidize the phosphite anion to phosphate one. Such a hypothesis has some weak points: (a) in our experiments we did not observe iodosobenzene formation; (b) the $>P—O^-$ anion oxidation by iodosobenzene is a much slower process [6] than the diisopropyl phosphate formation in the reaction under investigation; (c) the known diacyloxyiodobenzenes do not react with the nucleophiles on the carbonyl carbon atom (they are not acylating agents). It is noteworthy that the reaction between sodium salts of secondary phosphine oxides and diacetoxyiodobenzene in THF gives a complex mixture of products.



SCHEME 3



SCHEME 4



SCHEME 5

Reaction Between Triphenylphosphine or Trialkyl phosphites With Diacyloxyiodobenzenes

Taking into account the reactivity of the trivalent phosphorus nucleophiles toward **2a** and the formation of reactive intermediate **6**, we decided to check if diacyloxyiodobenzene/triphenylphosphine and diacyloxyiodobenzene/trialkyl phosphites systems will serve as condensation agents.

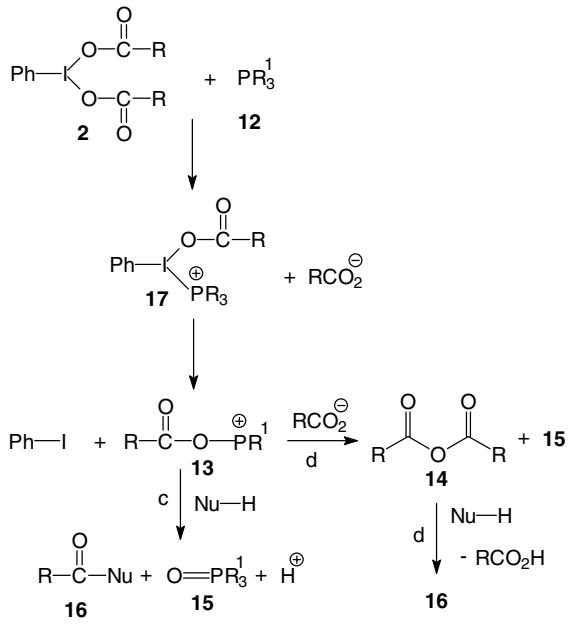
At first we investigated the reaction between diacyloxyiodobenzenes **2**, alcohols, and triphenylphosphine or trialkyl phosphites **12** (R^1 = Ph, OMe, O-*i*-Pr). It was found that this reaction is fast and furnishes the ester of the corresponding carboxylic acid **16** (Nu = OMe) with almost quantitative yield, triphenylphosphine oxide or trialkyl phosphate **15** (R^1 = Ph, OMe, O-*i*-Pr) and iodobenzene (Scheme 6, Table 3). At this point one can argue that carboxylic ester can be formed in the reaction of diacyloxyiodobenzene with alcohol. In a blank experiment we dissolved diacetoxyiodobenzene in methanol and after the heating for 15 min up to boiling point of solvent, we distilled off the methanol from the reaction mixture obtaining pure starting material.

Furthermore, we discovered that diacyloxyiodobenzenes **2** in combination with triphenylphosphine or trialkyl phosphites **12** (R^1 = Ph, OMe, O-*i*-Pr) react smoothly with benzylamine affording excellent yields of corresponding *N*-benzyl amides **16** (Nu = $PhCH_2NH$). Because it is known that **2a** oxidizes primary amines to form a complicated mixture of products, in this second set of experiments diacyloxyiodobenzene **2** dissolved in chloroform was stirred for 10–20 min with 1 equiv of triphenylphosphine or trialkyl phosphites, followed by successive addition of 3 equiv of benzylamine. Aqueous work-up, followed by chromatography on a silica gel (radial chromatography), provided *N*-benzylamides **16** (Nu = $HNCH_2C_6H_5$) in very high yield (see Table 3).

Acylation of the nucleophilic reagents in the reaction under investigation may occur by pathway c and also by d (Scheme 6). In pathway c the activated species, that is, acyloxyphosphonium salts **13**

TABLE 2 Product Distribution of the Reaction Between Sodium Diisopropyl Phosphite **8** and Diacetoxyiodobenzene **2a** at Different Molar Ratios

Run	Ratio **8**/**2a**	Recov. **2a** (%)	Isolated Yield (%)		
			PhI	**9**	**4a**
15	1	43	51	37	91
16	2	0	95	38	96
17	3	0	92	90	90



SCHEME 6

TABLE 3 Reaction of Diacyloxyiodobenzene **2**/PR^1_3 System with Nucleophiles

					Yield (%)		
Run	*Ratio NuH/***2**	*R*	*PR^1_3*	*Nu–H*	**14**	**15**	**16**
18	3	CH_3	PPh_3	$PhCH_2NH_2$		100	94
19	3	CH_3	$P(OMe)_3$	$PhCH_2NH_2$			68
20	3	CH_3	$P(O\text{-}i\text{-}Pr)_3$	$PhCH_2NH_2$			66
21	3	C_6H_5	PPh_3	$PhCH_2NH_2$		84	85
22	1	C_6H_5	PPh_3	MeOH	18	79	75
23	3	C_6H_5	PPh_3	MeOH	5	96	86
24	5	C_6H_5	PPh_3	MeOH		94	96
25	3	C_6H_5	$P(OMe)_3$	$PhCH_2NH_2$			71
26	3	C_6H_5	$P(OMe)_3$	MeOH	24		70
27	3	C_6H_5	$P(O\text{-}i\text{-}Pr)_3$	$PhCH_2NH_2$			84
28	3	C_6H_5	$P(O\text{-}i\text{-}Pr)_3$	MeOH	31		60
29	6	4-$MeOC_6H_4$	PPh_3	$PhCH_2NH_2$		80	75
30	10	4-$MeOC_6H_4$	PPh_3	MeOH		85	73
31	6	4-$C_6H_5C_6H_4$	PPh_3	$PhCH_2NH_2$		94	87
32	6	2-naphthyl-	PPh_3	$PhCH_2NH_2$		72	86
33	6	9-anthracenyl-	PPh_3	$PhCH_2NH_2$		90	95
34	6	3-$CF_3C_6H_4$	PPh_3	$PhCH_2NH_2$		74	88
35	6	2-furanyl-	PPh_3	$PhCH_2NH_2$		73	82
36	2	2-$CH_3CO_2C_6H_4$	PPh_3	$PhCH_2NH_2$		88	77
37		PhCONHCH(*i*-Pr)-	$P(OMe)_3$				45
38		*t*-BuOCONHCH$_2$CH$_2$-	$P(OMe)_3$				23
39	3	2,4,6-$Me_3C_6H_2$	PPh_3	$PhCH_2NH_2$		94	61
40	3	2,4,6-$Me_3C_6H_2$	PPh_3	MeOH		96	88
41	3	2,4,6-$Me_3C_6H_2$	$P(OMe)_3$	$PhCH_2NH_2$			85
42	3	2,4,6-$Me_3C_6H_2$	$P(OMe)_3$	MeOH	56		30
43	3	2,4,6-$Me_3C_6H_2$	$P(O\text{-}i\text{-}Pr)_3$	$PhCH_2NH_2$			72
44	3	2,4,6-$Me_3C_6H_2$	$P(O\text{-}i\text{-}Pr)_3$	MeOH	52		44
45	15	2,4,6-$Me_3C_6H_2$	$P(O\text{-}i\text{-}Pr)_3$	MeOH	36		60

(formed from intermediate **17**) reacts with the nucleophile to yield acylated product **16**. On the other hand intermediate **13** may react with carboxylic acid anion to form carboxylic acid anhydride **14** (pathway d), which in the following reaction with nucleophile leads to the formation of acylated product **16**.

When this reaction was carried out in two separate steps, that is, preactivation of diacyloxyiodobenzene with PR_3 followed by addition of benzylamine, ^{1}H NMR spectroscopy revealed formation of carboxylic acid anhydrides. Furthermore we were able to demonstrate that the treatment of diacyloxyiodobenzene with trimethylphosphite produces carboxylic acid anhydride (Table 3, runs 37 and 38). Additionally, in a separate experiment the treatment of di(2,4,6-trimethylbenzoyloxy)iodobenzene with triphenylphosphine in chloroform during 2 h produced 2,4,6-trimetylbenzoic anhydride with 92% isolated yield. This finding indicates that amide **16** (Nu = $HNCH_2C_6H_5$) is formed via pathway d, using the preactivation protocol.

In some experiments, where in one pot procedure we treated dibenzoyloxyiodobenzene with 1 equiv of alcohol and 1 equiv of triphenylphosphine or trialkyl phosphite, beside esters as major products, we also isolated small amounts of benzoic anhydride (Table 3, runs 22, 23, 26, and 28), which can suggest that in this case also pathway d operates. On the other hand, we were able to demonstrate in a separate experiment that benzoic anhydride and MeOH in chloroform solution at the boiling point of the solvent do not produce methyl benzoate even after 1 h. However it is known that phosphines may catalyze alcohol acylation by carboxylic acids anhydrides [13]. In a separate experiment we treated benzoic anhydride with methanol in chloroform solution in the presence of triphenylphosphine; in this experiment also we did not observe methyl benzoate formation. The results of this set of experiments exclude the formation of ester in the reaction in focus via carboxylic acid anhydride as a major pathway and we believe that formation of esters **14** (Nu = OMe, OEt, O-*i*-Pr) in the discussed reaction proceed via the acyloxyphosphonium salts **13** (Scheme 6).

The anhydride isolated in some experiments (Table 3, runs 22, 23, 26, and 28) indicates that alcohol competes with carboxylic acid anion for intermediate **13**, but the reaction with alcohol is much faster.

If this scheme were correct, we would expect to find exclusively methyl benzoate among the products of the reaction carried out with an excess of methanol. This expectation was verified by experiment. We carried out reactions of 1 equiv of dibenzoyloxyiodobenzene with different amounts of methanol under standard conditions ($CHCl_3$, 60°C, 10 min). The results of this set of experiments are presented in Table 3 (runs 22–24). As one can see from the data presented in Table 3, the products distribution strongly depends on the ratio of dibenzoyloxyiodobenzene to methanol. In the case of molar ratios 1:1 and 1:3 (runs 22 and 23) methyl benzoate was isolated from the reaction mixture as a major product and benzoic anhydride as a minor one. The yield of methyl benzoate **16** (R = Ph; Nu = OMe) increased with the increase in concentration of methanol used. When the reaction of dibenzoyloxyiodobenzene was carried out with 5 equiv of methanol (run 24), only one major product was produced: methyl benzoate with 96% of isolated yield.

As indicated by the data collected in Table 3 the sterically hindered reagent 2,4,6-trimethylbenzoic acid has been shown to also give high yield of corresponding esters (runs 40, 42, 44, and 45) or amides (runs 39, 41, and 43). In the case of a higly sterically hindered carboxylic acid, i.e. the 2,4,6-trimethylbenzoic acid, from the reaction mixture we isolated 2,4,6-trimethylbenzoic acid anhydride, what is in full agreement with literature data [14,15] (runs 42, 44, 45).

CONCLUSION

The results of our experiments suggest that >P(O)H type acids react with diacyloxyiodobenzene in alcohol solution to yield intermediate **6**, which may participate in two competiting processes. The intermediate **6** may break into mixed anhydride **7** (an acylation agent) and iodobenzene (pathway a) or may react with alcohol (alcoholate anion) leading to >P(O)OR esters (pathway b).

Furthermore it was found that diacyloxyiodobenzene/PR_3 system may serve as an acylation agent. The acylation process in the reaction under investigation can proceed via carboxylic acid anhydride or acylphosphonium salt **17** depending on the protocol used.

EXPERIMENTAL

All reactions were carried out under argon atmosphere in dry solvents (THF was dried over potassium, chloroform over P_2O_5, and alcohols over magnesium). Chromatography was carried out on Silica Gel 60 (0.15–0.3 mm) Macherey Nagel®. ^{31}P NMR and ^1H NMR spectra were recorded with a Varian apparatus at 200 or 500 MHz. Diacetoxyiodobenzene was purchased from Avocado, other diacyloxyiodobenzenes were prepared by a method described in literature [16].

Reactions Between Diacetoxyiodobenzene **2a** *and* $R^1R^2P(O)H$ **1** *in Alcohols*

To the solution of **2a** (1 mmol, 0.322 g) in 5 ml of alcohol, 1 mmol of **1** (diisopropylphosphite, *O*-isopropylphenylphosphinate, di-*n*-hexylphosphine oxide, *tert*-butylphenylphosphine oxide) was added. The reaction mixture was stirred for 1 h (Table 1, runs 1 and 2 for 24 h) at the boiling point of the solvent. The solvent was removed in the vacuum and the residue was dissolved in 30 ml of ether and extracted with 5% aqueous $NaHCO_3$ solution (2 × 10 ml). The organic layer was dried over $MgSO_4$, filtered, and evaporated to give appropriate methyl or isopropyl ester. The water layer was acidified with conc HCl and extracted with ether (3 × 10 ml). The collected ether solutions were dried over $MgSO_4$, filtered, and evaporated to give phosphinic or phosphonic acid respectively. All products were characterized by ^1H NMR and ^{31}P NMR and compared with authentic samples. Yields are presented in Table 1.

Reactions Between Diacetoxyiodobenzene **2a** *and* $R^1R^2P(O)H$ **1** *in Alcohols in the Presence of an Alcoholate*

To the mixture of **2a** (1 mmol, 0.322 g) and sodium alcoholate (1 mmol) in 5 ml of alcohol, 1 mmol of **1** (diisopropylphosphite, *O*-isopropylphenylphosphinate, di-*n*-hexylphosphine oxide, *tert*-butylphenylphosphine oxide) was added. The reaction mixture was stirred for 1 h at the boiling point of the solvent. The solvent was removed in the vacuum and the residue was dissolved in 30 ml of ether and extracted with 5% $NaHCO_3$ water solution (2 × 10 ml). The organic layer was dried over $MgSO_4$, filtered, and evaporated to give appropriate methyl or isopropyl ester. The water layer was acidified with conc HCl and extracted with ether (3 × 10 ml). The collected ether solutions were dried over $MgSO_4$, filtered, and evaporated to give phosphinic or phosphonic acid respectively. All products were characterized by ^1H NMR and ^{31}P NMR and compared with authentic samples. Yields are presented in Table 1.

Reactions Between Sodium Diisopropyl Phosphite **8** *and Diacetoxyiodobenzene* **2a** *at Different Ratios*

To a suspension of NaH (1.1, 2.2, or 3.3 mmol) in 5 ml of THF, diisopropylphosphite (1, 2, or 3 mmol) was added. When the evolution of hydrogen ceased, **2a** (1 mmol, 0.322 g) was added. The reaction mixture was stirred for 1 h at room temperature, the solvent was removed in vacuum, and the residue was dissolved in 30 ml of ether and extracted with 5% $NaHCO_3$ water solution (2 × 10 ml). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was separated by chromatography on silica gel using acetone/$CHCl_3$ as eluent. The yields of iodobenzene and diisopropyl 1-(diisopropoxyphosphinyl)ethyl phosphate are presented in Table 2. The water layer was acidified with conc HCl and extracted with ether (4 × 10 ml). The collected ether solutions were dried over $MgSO_4$, filtered, and evaporated to give diisopropylphosphate. All products were characterized by ^{1}H NMR and ^{31}P NMR and compared with authentic sample. Unreacted amounts of $PhI(OAc)_2$ in performed experiments were estimated by iodometric titration.

Run 15: diisopropyl 1-(diisopropoxyphosphinyl)-ethyl phosphate (0.25 mmol, 0.094 g); ^{31}P NMR ($CDCl_3$) $\delta = 19.67$ (d, $^3J_{PP} = 35$ Hz), -0.92 (d, $^3J_{PP} = 35$ Hz); Iodobenzene (0.51 mmol, 0.104 g).

Run 16: diisopropyl 1-(diisopropoxyphosphinyl)-ethyl phosphate (0.51 mmol, 0.191 g); Iodobenzene (0.95 mmol, 0.193 g).

Run 17: diisopropyl 1-(diisopropoxyphosphinyl)-ethyl phosphate (0.90 mmol, 0.336 g); Iodobenzene (0.9 mmol, 0.183 g).

Reactions Between Diacyloxyiodobenzene **2** *and* PR^1_3 **12** *in the Presence of Methanol*

To a mixture composed of **2** (1 mmol) and methanol (1, 3, 5, 10, 15 mmol) in 5 ml of chloroform, PR^1_3 (1 mmol) (triphenylphosphine, trimethylphosphite, or triisopropylphosphite) was added. The reaction mixture was stirred at the boiling point of the solvent for 1 h. Then the solvent was removed in vacuum, the residue was dissolved in 30 ml of ether and extracted with 5% $NaHCO_3$ water solution (2 × 10 ml). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was separated by chromatography on silica gel using acetone/hexane as eluent to give esters and anhydrides. All products were characterized by ^{1}H NMR and compared with authentic samples. Yields are presented in Table 3.

Preparation of Amides by Acylating System: Diacyloxyiodobenzene **2** *and* PR^1_3 **12**

To a solution of **2** (1 mmol) in 5 ml of chloroform, PR^1_3 (1 mmol) (triphenylphosphine, trimethylphosphite, or triisopropylphosphite) was added. Reaction mixture was stirred at the boiling point of the solvent for 1 h, and then benzylamine (2, 3, or 6 mmol) was added. The reaction mixture was stirred for additional 10 min, solvent was removed in vacuum, and residue was dissolved in 30 ml in ether and extracted with 5% $NaHCO_3$ water solution (2 × 10 ml). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was separated by chromatography on silica gel using CH_2Cl_2/MeOH as eluent to give amides. All amides were characterized by ^{1}H NMR and compared with authentic sample. Yields are presented in Table 3.

Carboxylic Acid Anhydrides **14**

To a solution of diacyloxyiodobenzene (1 mmol) in 5 ml of chloroform, trimethylphosphite (1 mmol, 0.124 g) was added. The reaction mixture was stirred at the boiling point of the solvent for 1 h. The solvent was removed in vacuum; the residue was disolved in 30 ml of ether and extracted with 5% $NaHCO_3$ water solution (2 × 10 ml). The organic layer was dried over $MgSO_4$ filtered, and evaporated to give anhydride.

(*S*)-2-benzoylamino-3-methyl-butyric acid anhydride (0.45 mmol, 0.190 g); ^{1}H NMR ($CDCl_3$) $\delta = 0.86$ (d, $^3J = 6.78$ Hz, 3H), 0.99 (d, $^3J = 6.83$ Hz, 3H), 2.19–2.22 (m, 1H), 4.12 (d, $^3J = 4.83$ Hz, 1H), 7.26–7.34 (m, 3H), 7.38–7.42 (m, 1H), 7.84–7.88 (m, 2H).

3-*tert*-butoxycarbonylamino-propionic acid anhydride (0.23 mmol, 0.083 g); ^{1}H NMR ($CDCl_3$) $\delta =$ 1.36 (s, 9H), 2.62 (t, $^3J = 5.86$ Hz, 2H), 3.35 (t, $^3J =$ 5.86 Hz, 2H), 7.63 (s, 1H).

2,4,6-trimethylbenzoic acid anhydride (0.95 mol, 0.294 g), m.p. 102–104°C; ^{1}H NMR ($CDCl_3$) $\delta = 2.31$ (s, 3H), 2.43 (s, 6H), 6.90 (s, 2H).

REFERENCES

[1] Stang, P. J.; Zhdankin, V. V. Chem Rev 1996, 96, 1123.
[2] Varvoglis, A. Tetrahedron 1997, 53, 1179.
[3] Foss, W. L.; Wejch, J. A.; Lermontov, S. A.; Luchenko, I. F. Zh Obshch Khim 1978, 48, 1713.
[4] Alcock, N. W.; Countryman, R. M.; Esperas, S.; Sawyer, J. F. J Chem Soc, Dalton Trans 1979, 854.
[5] Koser, G. F.; Lodaya, J. S.; Ray, D. G., III; Kokol, P. B. J Am Chem Soc 1988, 110, 2987.
[6] Makowiec, S.; Rachon, J. Phosphorus Sulfur, Silicon 2002, 177, 941.
[7] Witt, D.; Rachon, J. Heteroat Chem 1996, 7, 359.

[8] Witt, D.; Ossowski, T.; Rachon, J. Heteroat Chem 1999, 10, 431.
[9] Fitch, S. J.; Moedritzer, K. J Am Chem Soc 1962, 84, 1876.
[10] Nicholson, D. A.; Vaughn, H. J Org Chem 1971, 36, 3843.
[11] Ruel, R.; Bouvier, J.-P.; Young, R. N. J Org Chem 1995, 60, 5209.
[12] Lecouvey, M.; Leroux, Y. Hetaroatom Chem 2000, 11, 556.
[13] Vedejs, E.; Bennett, N. S.; Conn, L. M.; Diver, S. T.; Gingras, M.; Lin, S.; Oliver, P. A.; Peterson, M. J. J Org Chem 1993, 58, 7286.
[14] Kunieda, T.; Higuchi, T.; Abe, Y.; Hirobe, M. Tetrahedron 1983, 39, 3253.
[15] Kim, S.; Lee, J. I.; Kim, Y. C. J Org Chem 1985, 50, 560.
[16] Merkushev, E. B.; Novikov, A. N.; Makarchenko, S. S.; Moskalchuk, A. S.; Glushkova, V. V.; Kogai, T. I.; Polyakova, L. G. Zh Org Khim 1975, 11, 1259.