

## Phosphonium-Iodonim Ylides in Nucleophilic Substitution Reactions

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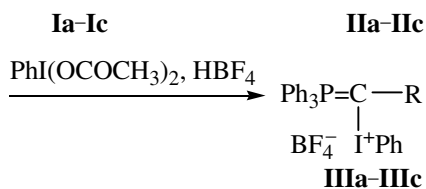
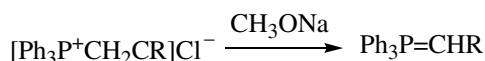
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**Abstract**—Properties of mixed phosphonium-iodonium ylides were investigated, and the compounds were shown to be capable to behave as O-nucleophiles in nucleophilic substitution reactions.

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Three-coordinated compounds of polyvalent iodine are well known already for a century. Within the last fifteen years new reagents of polyvalent iodine have been obtained whose application provides novel synthetic opportunities for the fine organic synthesis [1–12]. The utilization of hypervalent iodine compounds in the synthesis of many classes of various functionally substituted compounds attract the interest to attempts of preparation and reactivity studies of mixed iodonium-phosphonium ylides [13–15].

Starting with phosphonium salts **Ia–Ic** through an intermediate formation of ylides **IIa–IIc** a synthesis was performed of phenyliodoniumcarboethoxy- (**IIIa**), phenyliodoniumcarbomethoxy- (**IIIb**), and phenyliodoniumcyanomethylenetriphenylphosphorane (**IIIc**) borofluorides.



R = COOC<sub>2</sub>H<sub>5</sub> (**a**), COOCH<sub>3</sub> (**b**), CN (**c**).

The synthesis can be carried out both by isolating intermediate ylide **II** and by successive addition of the reagents without isolation of ylide **II**. The yield of

carboethoxy ylide **IIIa** reached only 40% in reaction without isolation of intermediate ylide **II** whereas in the two-stage reaction the yield of the iodonium ylide grew to 80%. We failed to obtain carbomethoxy ylide **IIIb** without separation of intermediate ylide **IIb**, but the two-stage reaction made it possible to prepare the target product in an overall yield 75%. Cyano-substituted ylide **IIIc** can be prepared by both methods but in the one-stage procedure the final yield of the mixed ylide **IIIc** is higher by 20%.

The structure of ylides **IIIa–IIIc** was confirmed by IR and NMR spectra and elemental analysis. In the <sup>1</sup>H NMR spectra of ylides **IIIa** and **IIIb** the signals of the ethyl and methyl groups appeared as very broad lines of low intensity at room temperature, and they start to resolve only over and below room temperature. For instance, the best resolution of these signals was attained at 60°C, and the resonances got their clear characteristic pattern: triplet and quartet for ethyl, narrow singlet for methyl group (Table 1).

At the same time on cooling to –40°C the ethoxy group of ylide **IIIa** appears in the spectrum as superimposed two triplets and two quartets [17], the methoxy group of ylide **IIIb**, as two singlets. These findings indicate the existence of a dynamic equilibrium between two interconverting forms of the ylides.

The temperature dependence characteristic of exchange processes was also observed in the <sup>13</sup>C and <sup>31</sup>P NMR spectra (Tables 2 and 3).

The signals in the spectra of ylide **IIIa** coalesce at 19°C permitting estimation of the activation energy of the dynamic process at Δ*G*<sub>292</sub> 57 kJ mol<sup>–1</sup>.

**Table 1.** Chemical shifts ( $\delta$ , ppm) in the  $^1\text{H}$  NMR spectra of ylides **IIIa–IIIc** at various temperatures

Compound no.	Solvent (temperature, °C)	Group		
		CH <sub>2</sub>	CH <sub>3</sub>	Ph
<b>IIIa</b>	CDCl <sub>3</sub> (20)	4.075 br.s	1.002 br.s	7.3–7.8 m
<b>IIIa</b>	CD <sub>3</sub> CN (60)	4.126 q	0.937 t	7.4–7.8 m
<b>IIIa</b>	CDCl <sub>3</sub> (–40)	4.150 q (major) 3.845 q (minor)	1.315 t (major) 0.441 t (minor)	7.3–7.8 m
<b>IIIb</b>	CD <sub>3</sub> CN (20)		3.55 br.c	7.4–7.8 m
<b>IIIb</b>	CD <sub>3</sub> CN (74)		3.55 s	7.4–7.8 m
<b>IIIb</b>	CD <sub>3</sub> CN (–35)		3.66 s (major) 3.26 s (minor)	7.4–7.8 m
<b>IIIc</b>	CD <sub>3</sub> CN (20)			7.2–7.8 m

**Table 2.** Chemical shifts in the  $^{13}\text{C}$  and  $^{31}\text{P}$  spectra ( $\delta$ , ppm) of ylide **IIIa** at various temperatures (in CD<sub>3</sub>CN)

Temperature, °C	$\text{C}^I$ ( $J_{\text{C-P}}$ )	CO ( $J_{\text{C-P}}$ )	CH <sub>2</sub>	CH <sub>3</sub>	Ph <sub>3</sub> P, ( $J_{\text{C-P}}$ ), [PhI]				$^{31}\text{P}$
					$\text{C}^i$	$\text{C}^o$	$\text{C}^m$	$\text{C}^p$	
–45	24.48 (123.5 Hz) (major)	167.22 (15.4 Hz)	62.01	14.55	124.16 (94.5 Hz) a	134.33 (10.6 Hz) [133.06]	130.07 (12.8 Hz) [131.47]	134.52 [131.95]	29.43
	30.92 (109.2 Hz) (minor)	167.19 (10.6 Hz)	61.95	13.55	123.59 (94.7 Hz) a	134.33 (10.6 Hz) [132.96]	130.07 (12.8 Hz) [131.41]	134.52 [131.95]	
55	b	168.35 (13.1 Hz)	62.74	14.66	125.05 (96.6 Hz) [119.05]	134.77 (10.5 Hz) [134.17]	130.71 (12.9 Hz) [132.73]	135.13 [133.32]	28.9 br.s

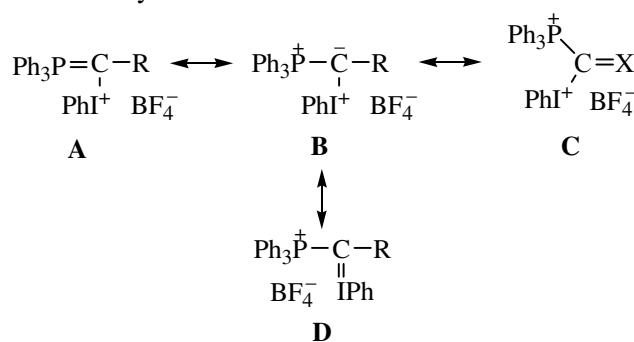
<sup>a</sup> The signal is overlapped by a strong signal of the CN group of the solvent. <sup>b</sup> The signal was not observed.

**Table 3.** Chemical shifts in the  $^{13}\text{C}$  and  $^{31}\text{P}$  spectra ( $\delta$ , ppm) of ylides **IIIb** and **IIIc** at various temperatures

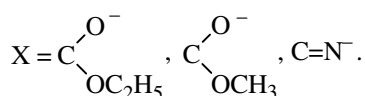
Compd. no.	Solvent (temperature, °C)	$\text{C}^I$ ( $J_{\text{C-P}}$ )	CO ( $J_{\text{C-P}}$ )	CH <sub>3</sub>	CN ( $J_{\text{C-P}}$ )	Ph <sub>3</sub> P, ( $J_{\text{C-P}}$ ), [PhI]				$^{31}\text{P}$
						$\text{C}^i$	$\text{C}^o$	$\text{C}^m$	$\text{C}^p$	
<b>IIIb</b> (major)	CD <sub>3</sub> CN (–40)	24.79 (123.6 Hz)	168.25 (15.7 Hz)	53.05		123.45 (94.6 Hz) a	134.35 (10.4 Hz) [133.35]	130.08 (12.8 Hz) [132.50]	134.55 (2.8 Hz) [132.06]	29.43
<b>IIIb</b> (minor)		31.93 (109.7 Hz)	168.33 (11.0 Hz)	52.74		124.10 (94.7 Hz) a	134.29 (10.4 Hz) [132.96]	130.10 (12.8 Hz) [131.41]	134.55 (2.8 Hz) [131.95]	
<b>IIIb</b>	CD <sub>3</sub> CN (55)	b	168.58 (14.3 Hz)	53.17		124.40 (94.7 Hz) [118.86]	134.77 (10.4 Hz) [134.17]	130.53 (12.8 Hz) [132.73]	134.83 (2.8 Hz) [132.98]	29.05 br.s
<b>IIIc</b>	DMSO- <i>d</i> <sub>6</sub> (25)	0.01 (123.9 Hz)			119.45 (2.8 Hz)	119.85 (93.0 Hz) [118.76]	133.58 (10.4 Hz) [133.05]	129.92 (12.7 Hz) [131.25]	134.59 (2.8 Hz) [131.62]	25.7 (CD <sub>3</sub> CN)

<sup>a</sup> The signal is overlapped by a strong signal of the CN group of the solvent. <sup>b</sup> The signal was not observed.

The structure of ylides **III** may be represented as a resonance hybrid of structures **A–D**.

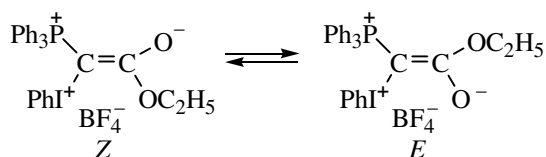


R = COOC<sub>2</sub>H<sub>5</sub>, COOCH<sub>3</sub>, CN;



Just the significant contribution of structure **C** determines the considerably high barrier to the rotation around the bond C–COOR (and C–CN). The fairly high shielding of the ylide carbon in the <sup>13</sup>C NMR spectra indicates also a significant contribution of resonance structure **B** (Tables 2 and 3).

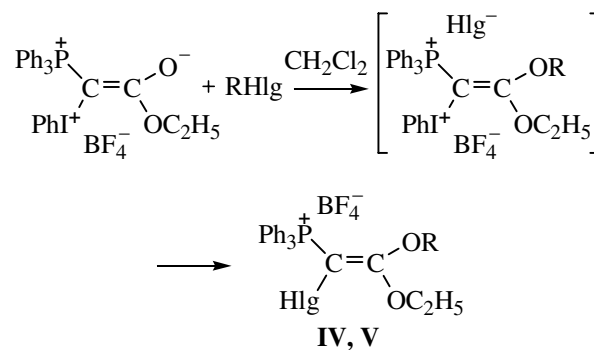
Thus the dynamic process we observe in solution may be represented by an example of ylide **IIIa** as an equilibrium between *Z*- and *E*-isomers.



The assignment of the stereoisomers was done based on the published data concerning <sup>13</sup>C NMR spectra of phosphorus ylides [16] which had established that the <sup>1</sup>J<sub>C–P</sub> and <sup>2</sup>J<sub>C–P</sub> constants in the isomer with the *trans*-location of PPh<sub>3</sub> and Oalk groups (*Z*-isomer in our case) are larger than those of the *cis*-isomer (*E*-isomer in our case). Hence the *Z*-isomer is somewhat more stable than *E*-isomer as has been confirmed by X-ray crystallography [17].

We investigated nucleophilic substitution reactions applying as a reagent mixed ylide **IIIa**. In the reactions of nucleophilic substitutions studied (alkylation, silylation, and acylation) this compound behaved as an O-nucleophile.

For instance, the alkylation of ylide **IIIa** with methyl iodide or ethyl bromide gave rise to esters **IV** and **V** respectively.

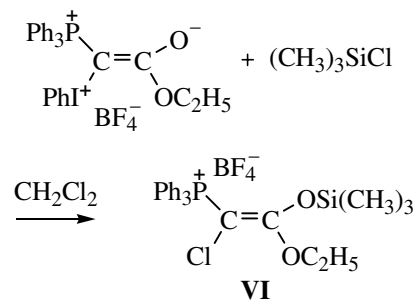


R = CH<sub>3</sub>, Hlg = I (**IV**); R = C<sub>2</sub>H<sub>5</sub>, Hlg = Br (**V**).

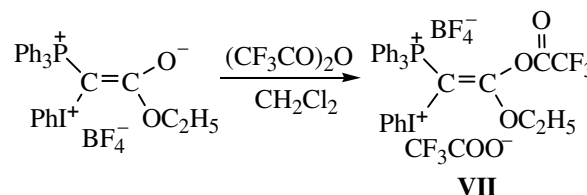
The alkylation by alkyl halides gave exclusively products of O-alkylation. Therewith we quantitatively isolated iodobenzene evidencing the occurrence of a nucleophilic substitution of iodonium fragment by the halide anion liberated in the course of the process; consequently, the reaction proceeded simultaneously at two reaction centers.

The alkylation with the methyl iodide is a fast reaction (3 h) with a quantitative yield of compound **IV**, but alkylation with ethyl bromide is considerably slower and gave a lower yield of the product **V** (50%), apparently due to the common decrease in the reactivity of ethyl bromide compared to methyl iodide because of the more difficult sterical accessibility of the electrophilic reaction site in the former.

We demonstrated that ylide **IIIa** also acted as the O-nucleophile in the reaction with trimethylsilyl chloride.



Acylation of ylide **IIIa** with trifluoroacetic anhydride under mild conditions gave rise to compound **VII** retaining in its structure the iodonium fragment.



The structure of compound **VII** synthesized was proved by IR and NMR spectroscopy. For compound **VII** a mass spectrum (MALDI) was also measured where ions were present of mass 761 [ $M - \text{BF}_4$ ]<sup>+</sup> and 648 [ $M - \text{BF}_4 - \text{CF}_3\text{COO}$ ]<sup>+</sup>.

## EXPERIMENTAL

<sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were registered on a spectrometer Bruker Avance 400 (operating frequency 400 MHz) using TMS as internal reference. IR spectra were recorded on a spectrophotometer UR-20 from solutions in tetrachloromethane. Elemental analysis was performed on Vario-II CHN-analyzer. Mass spectra (MALDI) were measured on Autoflex II (Bruker Daltonics) instrument. The reactions progress was monitored and the purity of chromatographically separated compounds was checked by TLC on Silufol plates.

**Phenyliodoniumcarboethoxymethylenetriphenylphosphorane borofluoride (IIIa).** *a.* To 5 ml of anhydrous methanol was gradually added 0.01 gram-atom of sodium metal, and after its complete dissolution a solution of 0.01 mol of phosphonium salt **Ia** in 5 ml of anhydrous methanol was dropwise added. The reaction mixture was cooled with ice water for 1 h to achieve complete precipitation of sodium chloride. The solution of ylide **IIa** was filtered off from the sodium chloride precipitate, cooled to 0°C, and a solution of 0.01 mol of phenyliodoso acetate in 8 ml of anhydrous methanol was added maintaining the temperature of the reaction mixture below 0°C. Then 0.01 mol of 40% HBF<sub>4</sub> solution was added maintaining the temperature of the reaction mixture at 0°C. The solution was stirred at this temperature for 1 h, then 5 ml of ethyl ether was added, and the stirring was continued for 1 h more. The separated precipitate was filtered off, washed with ether, and dried in air. Yield 40%, mp 190–191°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1600, 1570, 1130–980. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN),  $\delta$ , ppm: 1.0 br.s (3H, CH<sub>3</sub>), 4.0 br.s (2H, OCH<sub>2</sub>), 7.3–7.8 m (15H<sub>arom</sub>). <sup>31</sup>P NMR spectrum (CD<sub>3</sub>CN),  $\delta$ , ppm: 28.9 s. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>CN),  $\delta$ , ppm: 14.66 s (CH<sub>3</sub>), 62.74 s (OCH<sub>2</sub>), 119.05 s (C<sup>i</sup>), 125.05 d (C<sup>i</sup>,  $J_{\text{CP}}$  96.6 Hz), 130.71 d (C<sup>m</sup>,  $J_{\text{CP}}$  12.9 Hz), 132.73 s (C<sup>m</sup>), 133.32 s (C<sup>p</sup>), 134.17 s (C<sup>o</sup>), 134.77 d (C<sup>o</sup>,  $J_{\text{CP}}$  10.5 Hz), 135.13 s (C<sup>p</sup>), 168.35 d (C=O,  $J_{\text{CP}}$  13.1 Hz). Found, %: C 52.44; H 3.89. C<sub>28</sub>H<sub>25</sub>BF<sub>4</sub>IO<sub>2</sub>P. Calculated, %: C 52.66; H 3.92.

*b. Reaction with isolation of carboethoxymethylenetriphenylphosphorane (IIa).* To a solution of 0.013 mol of carboethoxymethylenetriphenylphosphonium chloride (**Ia**) in 10 ml of water was added 5 ml of 50% NaOH

solution till pH 8. The separated precipitate was filtered off, washed with water, dried, and recrystallized from ethanol (15 ml), washed with ether, and dried. Yield of ylide **IIa** 3.5 g (77%), mp 112–113°C. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 1.05 br.s (3H, CH<sub>3</sub>), 2.75 br.s (1H, CH), 3.9 q (2H, CH<sub>2</sub>), 7.2–7.8 m (15H<sub>arom</sub>). <sup>31</sup>P NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 19.1 s. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 14.61 s (CH<sub>3</sub>), 29.59 d (C<sup>i</sup>,  $J_{\text{CP}}$  127.7 Hz), 57.59 d (OCH<sub>2</sub>,  $J_{\text{CP}}$  2.2 Hz), 126.18 d (C<sup>i</sup>,  $J_{\text{CP}}$  91.6 Hz), 126.9 (C<sup>m</sup>,  $J_{\text{CP}}$  12.2 Hz), 131.01 d (C<sup>o</sup>,  $J_{\text{CP}}$  9.9 Hz), 132.25 d (C<sup>p</sup>,  $J_{\text{CP}}$  2.7 Hz), 168.81 d (C=O,  $J_{\text{CP}}$  12.1 Hz).

To a solution of 3.5 g (0.01 mol) of ylide **IIa** in 5 ml of methanol cooled to 0°C was added a solution of 0.01 mol of phenyliodoso acetate in 10 ml of methanol maintaining with the rate of addition the temperature of the mixture below 5°C, then 2.5 ml of 40% HBF<sub>4</sub> solution was added maintaining the temperature of the reaction mixture at 0–5°C. The stirring was continued for 1 h, 10 ml of ethyl ether was added, and the mixture was stirred for 1 h more. The separated precipitate was filtered off and washed with ether. Yield of compound **IIIa** 5.3 g (85%), mp 190–191°C.

**Carbomethoxymethylenetriphenylphosphorane (IIb).** To a solution of 5 g (0.013 mol) of carbomethoxymethylenetriphenylphosphonium chloride (**Ib**) in 10 ml of water was added 5 ml of 50% NaOH solution till pH 8. The separated precipitate was filtered off, washed with water, dried, and recrystallized from ethanol (15 ml), washed with ether, and dried. Yield 3.5 g (81%), mp 162–163°C. <sup>31</sup>P NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 17.8 s. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 29.78 d (C<sup>i</sup>,  $J_{\text{CP}}$  126.7 Hz), 49.67 d (OCH<sub>3</sub>,  $J_{\text{CP}}$  2.6 Hz), 128.18 d (C<sup>i</sup>,  $J_{\text{CP}}$  91.2 Hz), 129.02 d (C<sup>m</sup>,  $J_{\text{CP}}$  12.2 Hz), 130.08 d (C<sup>p</sup>,  $J_{\text{CP}}$  3.0 Hz), 133.20 d (C<sup>o</sup>,  $J_{\text{CP}}$  10.1 Hz), 171.96 d (C=O,  $J_{\text{CP}}$  12.7 Hz).

**Phenyliodoniumcarbomethoxymethylenetriphenylphosphorane borofluoride (IIIb).** To a solution of 3.5 g (0.01 mol) of ylide **IIb** in 5 ml of methanol cooled to 0°C was added a solution of 3.25 g (0.01 mol) of phenyliodoso acetate in 10 ml of methanol maintaining with the rate of addition the temperature of the mixture below 5°C, then 2.5 ml of 40% HBF<sub>4</sub> solution was added maintaining the temperature of the reaction mixture at 0–5°C. The stirring was continued for 1 h, 10 ml of ethyl ether was added, and the mixture was stirred for 1 h more. The separated precipitate was filtered off and washed with ether. Yield 4.7 g (75%), mp 199–200°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1600, 1570, 1486. <sup>1</sup>H NMR spec-

trum (CD<sub>3</sub>CN),  $\delta$ , ppm: 3.55 br.s (3H, OCH<sub>3</sub>), 7.4–7.8 m (15H<sub>arom</sub>). <sup>31</sup>P NMR spectrum (CD<sub>3</sub>CN),  $\delta$ , ppm: 29.08 s. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>CN),  $\delta$ , ppm: 53.17 s (OCH<sub>3</sub>), 118.86 s (C<sup>i</sup>), 124.40 d (C<sup>i</sup>, J<sub>CP</sub> 94.7 Hz), 130.53 (C<sup>m</sup>, J<sub>CP</sub> 12.8 Hz), 132.73 s (C<sup>m</sup>), 132.98 s (C<sup>p</sup>), 134.17 s (C<sup>o</sup>), 134.77 d (C<sup>o</sup>, J<sub>CP</sub> 10.4 Hz), 134.83 d (C<sup>p</sup>, J<sub>CP</sub> 2.8 Hz), 168.53 d (C=O, J<sub>CP</sub> 14.3 Hz). Found, %: C 52.35; H 3.92. C<sub>27</sub>H<sub>23</sub>BF<sub>4</sub>IO<sub>2</sub>P. Calculated, %: C 52.66; H 3.90.

**Phenyliodoniumcyanomethylenetriphenylphosphorane borofluoride (IIIc).** To 5 ml of anhydrous methanol was gradually added 0.01 gram-atom of sodium metal, and after its complete dissolution a solution of 0.01 mol of phosphonium salt **Ia** in 5 ml of anhydrous methanol was dropwise added. The reaction mixture was cooled with ice water for 1 h to achieve complete precipitation of sodium chloride. The solution of ylide **Ic** was filtered off from the sodium chloride precipitate, cooled to 0°C, and a solution of 0.01 mol of phenyliodoso acetate in 8 ml of anhydrous methanol was added maintaining the temperature of the reaction mixture below 0°C. Then 0.01 mol of 40% HBF<sub>4</sub> solution was added maintaining the temperature of the reaction mixture at 0°C. The solution was stirred at this temperature for 1 h, then 5 ml of ethyl ether was added, and the stirring was continued for 1 h more. The separated precipitate was filtered off, washed with ether, and dried in air. Yield 70%, mp 190–191°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1150 (BF<sub>4</sub><sup>-</sup>), 2160 (CN). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 7.2–7.8 m (15H<sub>arom</sub>). <sup>31</sup>P NMR spectrum (CH<sub>3</sub>CN),  $\delta$ , ppm: 25.7 s. <sup>13</sup>C NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 0.01 d (C<sup>i</sup>, J<sub>CP</sub> 123.9 Hz), 118.76 s (C<sup>i</sup>), 119.45 d (CN, J<sub>CP</sub> 2.8 Hz), 119.85 d (C<sup>i</sup>, J<sub>CP</sub> 93.0 Hz), 129.92 d (C<sup>m</sup>, J<sub>CP</sub> 12.7 Hz), 131.25 s (C<sup>m</sup>), 131.62 s (C<sup>p</sup>), 133.05 s (C<sup>o</sup>), 133.58 d (C<sup>o</sup>, J<sub>CP</sub> 10.4 Hz), 134.59 d (C<sup>p</sup>, J<sub>CP</sub> 2.8 Hz).

**Alkylation of ylide IIIa. General procedure.** To a solution of 0.2 g (0.314 mmol) of ylide **IIIa** in 5 ml of anhydrous dichloromethane 0.628 mmol of alkyl halide was added. The reaction mixture was stirred under argon flow. The end of reaction was established by disappearance of ylide **IIIa** (TLC monitoring). The solvent was removed on a rotary evaporator. The residue was washed with anhydrous ethyl ether.

**(2-Ethoxy-1-iodo-2-methoxyvinyl)triphenylphosphonium borofluoride (IV).** Reaction time 6 h. Yield 0.18 g (100%). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1080 (BF<sub>4</sub><sup>-</sup>), 1590 (C=C). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 1.00 t (3H, CH<sub>3</sub>), 3.38 s (3H, OCH<sub>3</sub>), 4.05 q (2H, CH<sub>2</sub>), 7.48–7.82 m (15H<sub>arom</sub>). <sup>31</sup>P NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 23.59 s. <sup>13</sup>C NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm:

–0.72 m (CI), 13.13 s (CH<sub>3</sub>), 59.73 s (OCH<sub>3</sub>), 63.07 s (OCH<sub>2</sub>), 130.41 d (C<sup>m</sup>, J<sub>CP</sub> 13.2 Hz), 133.98 d (C<sup>o</sup>, J<sub>CP</sub> 10.1 Hz), 135.55 d (C<sup>p</sup>, J<sub>CP</sub> 3.0 Hz), 164.81 m (CO).

**(1-Bromo-2,2-diethoxyvinyl)triphenylphosphonium borofluoride (V).** Reaction time 24 h. Yield 0.085 g (50%). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 0.94 t (3H, CH<sub>3</sub>), 1.22 t (3H, CH<sub>3</sub>), 4.02 m (4H, 2CH<sub>2</sub>), 7.75–7.89 m (15H<sub>arom</sub>). <sup>31</sup>P NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 25.79 s.

**[1-Chloro-2-ethoxy-2-[(trimethylsilyloxy)vinyl]triphenylphosphonium borofluoride (VI).** To a solution of 0.2 g (0.314 mmol) of ylide **IIIa** in 5 ml of anhydrous dichloromethane 0.034 g (0.314 mmol) of trimethylsilyl chloride was added. The reaction mixture was stirred for 4 h under argon flow. The end of reaction was established by disappearance of ylide **IIIa** (TLC monitoring). Yield 0.17 g (100%). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 0.07 d (3H, SiMe<sub>3</sub>), 0.23 d.d (6H, SiMe<sub>3</sub>), 1.06 t (3H, CH<sub>3</sub>), 4.12 q (2H, CH<sub>2</sub>), 7.70–7.92 m (15H<sub>arom</sub>). <sup>31</sup>P NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 29.37 s. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 0.05 s, 0.20 s (SiMe<sub>3</sub>), 13.47 s (CH<sub>3</sub>), 49.15 d (C<sup>i</sup>, J<sub>CP</sub> 54.9 Hz), 64.84 s (OCH<sub>2</sub>), 115.54 d (C<sup>i</sup>, J<sub>CP</sub> 87.0 Hz), 130.38 d (C<sup>m</sup>, J<sub>CP</sub> 13.2 Hz), 134.51 d (C<sup>o</sup>, J<sub>CP</sub> 11.0 Hz), 135.80 d (C<sup>p</sup>, J<sub>CP</sub> 2.9 Hz), 157.17 s (CO).

**(2-Ethoxy-1-{phenyl[(trifluoroacetyl)oxy]- $\lambda$ 3-iodanil}-2-[(trifluoroacetyl)oxy]-vinyl)triphenylphosphonium borofluoride (VII).** To a solution of 0.2 g (0.314 mmol) of ylide **IIIa** in 5 ml of anhydrous dichloromethane 0.132 g (0.628 mmol) of trifluoroacetic anhydride was added. The reaction mixture was stirred for 4 h under argon flow. The end of reaction was established by disappearance of ylide **IIIa** (TLC monitoring). The solvent was removed on a rotary evaporator. The residue was washed with anhydrous ethyl ether. Yield 0.2 g (80%). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1080 (BF<sub>4</sub><sup>-</sup>), 1445 (PC<sub>6</sub>H<sub>5</sub>), 1590 (C=C), 1750 (C=O). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 0.96 t (3H, CH<sub>3</sub>), 4.06 q, 4.10 q (2H, CH<sub>2</sub>), 7.70–7.92 m (15H<sub>arom</sub>). <sup>31</sup>P NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 27.37 s, 27.60 s. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 13.26 s (CH<sub>3</sub>), 64.97 s (OCH<sub>2</sub>), 69.51 d (C<sup>i</sup>, J<sub>CP</sub> 65.2 Hz), 113.66 d (C<sup>i</sup>, J<sub>CP</sub> 87.8 Hz), 130.28 s (C<sup>p</sup>), 130.70 d (C<sup>m</sup>, J<sub>CP</sub> 13.2 Hz), 134.32 s (C<sup>m</sup>), 134.42 d (C<sup>o</sup>, J<sub>CP</sub> 11.0 Hz), 136.46 d (C<sup>p</sup>, J<sub>CP</sub> 3.6 Hz), 137.46 s (C<sup>o</sup>), 161.47 s (C=O), 187 s (CO).

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