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I. P. Beletskaya on occasion of her jubilee

Synthesis and Structure of Mixed Phosphonium-iodonium Ylide

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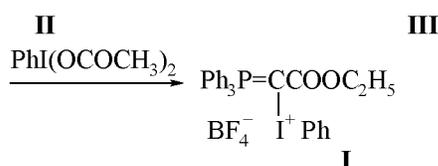
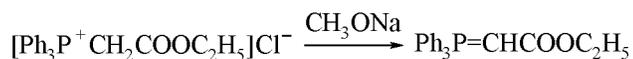
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Abstract—A mixed phosphonium-iodonium ylide, phenyliodoniummethoxycarbonylmethylenetriphenylphosphorane borofluoride, was synthesized. Its structure was established by means of X-ray diffraction analysis. Temperature dependence of ¹H, ¹³C, and ³¹P spectra of the ylide synthesized was investigated. A dynamic equilibrium between *Z* and *E*-isomers was observed.

A vigorous development of hypervalent iodine chemistry within the last decade is due to extension of application of compounds belonging to this important class as promising reagents for organic synthesis [1-12]. For instance, we have shown formerly the feasibility of using these reagents in preparation of organic triflates [3, 4, 7], perchlorates [3, 4, 5-9], azides [10], and the other types of functional derivatives [3, 4].

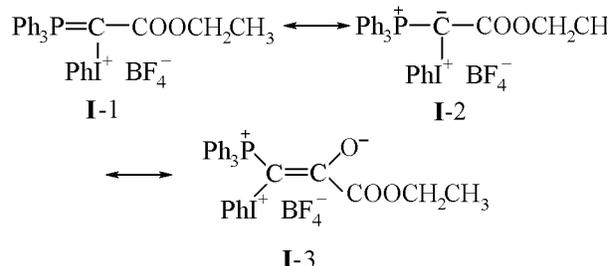
In the present study we investigated the synthesis and reactivity of mixed phosphonium-iodonium ylides of **I** type (a preliminary communication on this topic see [12]). Although several cases of mixed ylides preparation was reported [13, 14], their structure was not unambiguously proved. We synthesized phenyliodoniummethoxycarbonylmethylenetriphenylphosphorane borofluoride (**I**) proceeding from phosphonium salt **II** that was transformed into ylide **III** with subsequent replacement of hydrogen atom by iodonium fragment along a scheme:



The yield of ylide **I** was only 40% if the reaction was carried out without isolation of intermediate ylide

III; the two-stage procedure involving isolation of ylide **III** furnished iodonium ylide **I** in up to 80% yield.

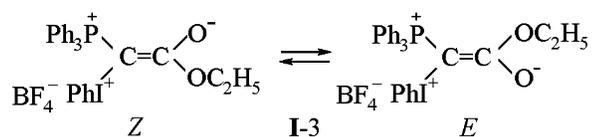
The structure and composition of ylide **I** were confirmed by IR and NMR spectra and by elemental analysis. In the ¹H NMR spectrum of ylide **I** recorded at room temperature the ethyl group signals are observed as broad lines of low intensity (Table 1). At 60°C and higher the signal of ethyl group appears as conventional triplet and quartet with corresponding intensities, and at -40°C as superimposed set of two triplets and quartets. These data reveal the existence of a dynamic equilibrium. We showed that ¹³C and ³¹P NMR spectra also have temperature dependence characteristic of exchange processes. In the ³¹P NMR spectrum taken in CD₃CN at -45°C appeared two separate signals of the interconverting structures (see Table 2). The peaks coalesce at 19°C that corresponds to activation energy of the dynamic process amounting to ΔG₂₉₂[‡] 57(2) kJ mol⁻¹. The equilibrium constant is not affected by solvent and equals 1.2 both in CD₃CN and CDCl₃. Parameters of the ¹³C NMR



spectrum of ylide **I** are sufficiently close to those of common triphenylphosphonium ylides [15].

The structure of ylide (**I**) may be represented as a resonance hybrid of structures (**I-1**), (**I-2**), and (**I-3**). Just the significant contribution of the structure of (**I-3**) type determines a notably high barrier to rotation around the C-COOR bond. The hampered rotation was observed in some triphenylphosphonium ylides before [16, 17]. The high shielding of ylide carbon observed in the ^{13}C NMR spectra reveals also a significant contribution of the resonance structure (**I-2**) (see Table 2).

Thus the dynamic process we observe may be represented as the *Z-E* equilibrium shown below:



Assignment of signals in spectra to stereoisomers was based on the published data on ^{13}C NMR for phosphor ylides [16]. It is established that in isomer with trans-location of the P and OR groups (in our case it is the *Z*-isomer) the value of coupling constants $^1J_{\text{C-P}}$ and $^2J_{\text{C-P}}$ is larger than in the *cis*-isomer (in our case it is *E*-isomer). Consequently the *Z*-(**I-3**) isomer is somewhat more stable than the *E*-(**I-3**) isomer. This is essentially confirmed by the data of X-ray diffraction study. Actually, the structure of ylide **I** in a crystal was established by X-ray diffraction analysis and was found to correspond to *Z*-(**I-3**)

Table 1. Chemical shifts in the ^1H NMR spectrum, δ , ppm, of ylide **I** at different temperature

Temperature, °C, solvent	CH ₂ ^a	CH ₃ ^a	Ph
-40 ^b CDCl ₃	major 4.150 q minor 3.845 q	1.315 t 0.441 t	7.3-7.8 m
40 CDCl ₃	4.075 br. peak	1.002 br. s	7.3-7.8 m
60 CD ₃ CN	4.126 q	0.937 t	7.4-7.8 m

^a $^3J_{\text{HH}}$ 7.1 Hz.

^b Isomers ratio 1.2:1.

formula. The general view of the molecule is presented on the figure.

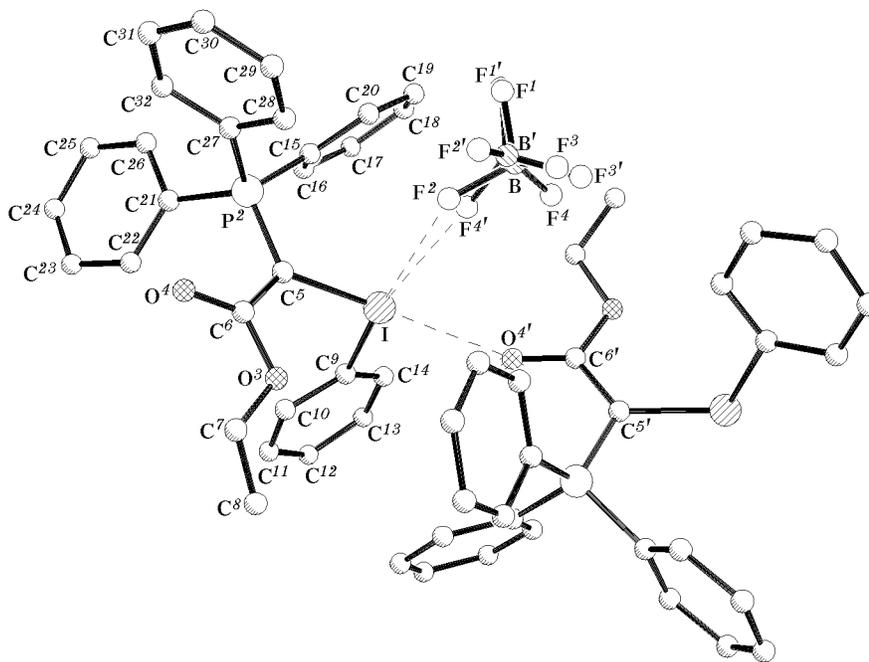
The structure of BF_4^- anion is disordered equally between two nearby positions (see the figure). In refining was used a constraint that all the B-F distances and FBF angles were equal; as a result the established length of the B-F bond was 1.34 Å, and the bond angle FBF was 109°. The length of bond C⁷-C⁸ 1.37(2) Å is considerably shorter than that of a common ethyl bond. This is due to strong thermal oscillations of the terminal ethyl group as also evidences the high value of the individual thermal factor for the C⁸ atom and significant anisotropy of its thermal oscillations. We failed to make a correct accounting for the thermal oscillation of the C⁸ atom because of insufficient quality of the crystal.

Table 2. Chemical shifts in ^{13}C and ^{31}P NMR spectra, δ , ppm, of ylide (**I**) at different temperature (in CD₃CN)

<i>T</i> , °C	C ¹	CO	CH ₂	CH ₃	Ph ₃ P (<i>J</i> _{C-P} , Hz), [PhI]				³¹ P
					C _{ipso}	C _o	C _m	C _p	
-45	24.48 (123.5)	167.22 (15.4)	62.01	14.55	124.16 (94.5) ^a	134.33 (10.6) [133.06]	130.07 (12.8) [131.47]	134.52 [131.95]	29.43 major
	30.92 (109.2)	167.19 (10.6)	61.95	13.55	123.59 (94.7) ^a	134.33 (10.6) [132.96]	130.07 (12.8) [131.41]	134.52 [131.95]	28.27 minor
55	^b	168.35 (13.1)	62.74	14.66	125.05 (96.6) [119.05]	130.10 (10.5) [134.17]	130.71 (12.9) [132.73]	135.13 [133.32]	28.9 br.s

^a Not observed, overlapped by strong signals of the CN group in solvent.

^b Not observed.



Structure of cation with indication of atoms supplemented by cation taking part in intermolecular bond, and of BF_4^- anion disordered by two positions.

Interestingly the atoms of cation P^2 , C^5 , I , C^6 , O^4 , O^3 , C^7 , C^{15} (see the figure) are located in the same plane within 0.07 Å. This fact confirms the significant contribution of the resonance structure (I-3). There are also additional structural arguments evidencing the latter. Firstly, the bond $\text{C}^5\text{-C}^6$ is 1.44(1) Å long; that shows its notably double character. On the contrary, the bond $\text{C}^5\text{-P}^2$ is 1.727(7) Å long. Taking into account the covalent radii in double bond of atoms C (0.655 Å) and P (1.000 Å) [18] we would expect that a double $\text{C}=\text{P}$ bond [resonance structure (I-1)] be about 1.655 Å long. A considerable elongation of this bond in *o*-tolyliodonium-*p*-phenylbenzoylmethylenetriphenylphosphorane (1.709 Å) [13], benzoyliodomethylenetriphenylphosphorane (1.713 Å) [19] as also in ylide I (1.727 Å) evidences a significant contribution to its structure of the resonance structure (I-3). The orientation of atoms O^4 and P^2 corresponds to the structure Z-(I-3).

Let us mention some more structural features of ylide I. Atom C^8 of the terminal ethyl group deviates from the above plane by torsional rotation around the $\text{C}^7\text{-O}^3$ bond through 29°. Atoms C^9 , C^{21} , and C^{27} go out of the plane by rotation around the bonds I-C^5 and $\text{C}^5\text{-P}^2$ through 81.5, 70.7, and 52.5°. The iodine atom where the most of the positive charge of the cation should be localized is involved in bonds I-C^9 2.136(7) Å long (with phenyl atom) and I-C^5

2.030(7) Å long. A similar distribution of bond lengths was found in *o*-tolyliodonium-*p*-phenylbenzoylmethylenetriphenylphosphorane [13]: I-C^9 2.094 Å, I-C^5 2.056 Å, $\text{C}^5=\text{P}$ 1.709 Å.

The molecules of ylide I in the crystal are packed in chains due to a shortened intermolecular contact $\text{I}\cdots\text{O}^4$ 2.815 Å (sum of van der Waals radii is equal to 3.17–3.32 Å [20]). The angles $\text{C}^6'\text{O}^4'\text{I}$ and $\text{C}^5'\text{IO}^4'$ are equal to 152.3 and 173.6° respectively indicating that between the unshared electron pair of the carbonyl oxygen and the I^+ atom exists not a simple Coulomb but also orbital $\sigma_{\text{I-C}^n}^*$ interaction that joins the cations into a chain.

Into the nearest environment of the iodine atom enter alternately the fluorine atoms $\text{F}^{2'}$ ($\text{I-F}^{2'}$ 3.211 Å) and $\text{F}^{4'}$ ($\text{I-F}^{4'}$ 2.943 Å). The sum of van der Waals radii of I and F is equal to 3.31–3.46 Å [20]. The angles $\text{C}^9'\text{IF}^{2'}$ and $\text{C}^9'\text{IF}^{4'}$ are 175.5 and 164.6°, also feasible for the $\sigma_{\text{I-C}^n}^*$ interaction. The atoms C^5 , C^9 , I , O^4 , $\text{F}^{2'}$, and $\text{F}^{4'}$ lie in the same plane constituting the planar coordination of I atom that is supplemented with a weak intramolecular interaction $\text{I}\cdots\text{O}^3$ 3.037 Å. The angles IO^3C^7 and IO^3C^6 are equal to 166.3 and 104.0°. Vector $\text{O}^3\text{-I}$ is oriented at an angle of 50.6° to the coordination plane. We established by preliminary experiments that ylide I enters into nucleophilic substitution reaction under mild conditions with such nucleophiles as azide and thiocyanate anions and thiourea. These studies and

Table 3. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) (for nonhydrogen atoms)

Atom no.	x	y	z	U^*_{eq}
I	2007(1)	2301(1)	1639(1)	50(1)
P ²	1166(1)	3045(1)	3743(2)	50(1)
O ³	3404(3)	2446(5)	3143(4)	75(2)
O ⁴	2836(3)	3054(4)	4551(4)	63(2)
C ⁵	2011(4)	2669(6)	3133(5)	48(2)
C ⁶	2768(4)	2752(6)	3686(7)	57(2)
C ⁷	4161(5)	2408(10)	3658(8)	97(4)
C ⁸	4588(9)	1666(12)	3224(14)	184(8)
C ⁹	1813(5)	613(6)	1716(7)	63(2)
C ¹⁰	2144(5)	115(7)	2513(8)	73(3)
C ¹¹	2051(6)	-967(7)	2520(9)	87(3)
C ¹²	1621(7)	-1539(8)	1777(10)	104(4)
C ¹³	1265(7)	-1004(8)	1026(9)	97(3)
C ¹⁴	1368(6)	92(7)	988(7)	75(3)
C ¹⁵	352(4)	3018(6)	2835(6)	52(2)
C ¹⁶	-183(5)	2123(7)	2728(9)	93(3)
C ¹⁷	-781(6)	2051(9)	1973(10)	116(4)
C ¹⁸	-858(6)	2887(8)	1347(7)	82(3)
C ¹⁹	-321(6)	3763(8)	1444(7)	81(3)
C ²⁰	278(5)	3873(7)	2173(7)	72(2)
C ²¹	786(5)	2157(6)	4721(6)	56(2)
C ²²	1218(4)	1360(5)	5101(6)	55(2)
C ²³	884(6)	711(7)	5883(7)	74(3)
C ²⁴	146(6)	837(8)	6233(7)	82(3)
C ²⁵	-303(6)	1620(8)	5875(8)	94(3)
C ²⁶	27(5)	2288(7)	5132(8)	87(3)
C ²⁷	1393(5)	4359(6)	4259(7)	60(2)
C ²⁸	1802(5)	5138(7)	3675(7)	68(2)
C ²⁹	1985(6)	6135(7)	4059(10)	92(3)
C ³⁰	1762(6)	6387(8)	5016(10)	89(3)
C ³¹	1361(7)	5633(9)	5592(9)	95(3)
C ³²	1163(6)	4601(7)	5245(7)	75(2)
B	2015(10)	5362(12)	555(13)	78(4)
F ¹	1380(13)	5850(20)	830(20)	129(3)
F ²	2268(19)	4822(19)	1336(19)	144(11)
F ³	2616(13)	6073(16)	244(19)	138(9)
F ⁴	1796(13)	4694(17)	-196(15)	170(9)
B ¹	2100(8)	5554(10)	732(11)	78(4)
F ²¹	2638(8)	6140(10)	1331(15)	141(7)
F ¹¹	1352(10)	5868(19)	860(20)	129(3)
F ³¹	2330(14)	5684(18)	-242(11)	155(9)
F ⁴¹	2084(14)	4524(11)	989(15)	124(10)
H ^{7A}	4479	3096	3626	
H ^{7B}	4059	2233	4364	
H ^{8A}	5093	1644	3578	
H ^{8B}	4697	1847	2529	

Table 3. (Contd.)

Atom no.	x	y	z	U^*_{eq}
H ^{8C}	4274	984	3261	
H ¹⁰	2421	500	3028	
H ¹¹	2284	-1323	3040	
H ¹²	1572	-2275	1782	
H ¹³	951	-1383	537	
H ¹⁴	1136	456	473	
H ¹⁶	-148	1554	3162	
H ¹⁷	-1128	1429	1898	
H ¹⁸	-1270	2854	866	
H ¹⁹	-357	4320	996	
H ²⁰	627	4497	2227	
H ²²	1725	1261	4835	
H ²³	1175	194	6157	
H ²⁴	-78	384	6736	
H ²⁵	-817	1690	6133	
H ²⁶	-257	2832	4901	
H ²⁸	1955	4987	3019	
H ²⁹	2267	6654	3659	
H ³⁰	1886	7070	5264	
H ³¹	1211	5804	6244	
H ³²	885	4087	5656	

the synthesis of ylide **I** analogs will be published elsewhere.

EXPERIMENTAL

¹H, ¹³C, and ³¹P NMR spectra were registered on spectrometer Bruker DPX-500 at operating frequencies 300.1, 75.4, and 121.5 MHz respectively. TMS served as internal reference in registering ¹H and ¹³C NMR spectra, for the ³¹P NMR spectra was used H₃PO₄ as external reference. Chromatographic monitoring was performed by TLC on Silufol plates.

X-ray diffraction study. Parameters of the unit cell of ylide **I** crystal and three-dimensional set of reflections intensities were obtained on diffractometer KUMA-DIFFRACTION KM-4 (Cu-K α -radiation, graphite monochromator) from an isometric single crystal of low quality of random form with a radius ~0.03 mm. Monoclinic crystal with the following unit cell parameters: *a* 16.529(4), *b* 12.715(2), *c* 13.227(7) Å, γ 96.41(2)°. *V* 2762(2) Å³, *M* 638.19, space group P 2₁/*n*, *Z* 4, *d*_{calc} 1.534 g cm⁻³.

Intensities of 3693 reflections were measured in the independent part of the reciprocal space ($2\theta \leq 81^\circ$) by procedure of $\omega/2\theta$ scanning. After exclusion

of the systematically quenched reflections the experimental set of the measured reflections was 2526 with $(I) > 2\sigma(I)$. The structure was solved by the direct method and was refined by full-matrix least-squares procedure with respect to F_2 with the use of SHELXL-97 software [21] in anisotropic approximation for the nonhydrogen atoms. All hydrogen positions were found geometrically and were not refined considering the quality of the crystal. The final coordinates and thermal factors of atoms in the structure under study are given in Table 3. The final value of R-factor 4.9% for 2526 reflections with $(I) > 2\sigma(I)$, parameter "good of fit" equals to 0.996, the structure of anion and cation are given on the figure.

Purification of solvents. Methanol. To 1 l of methanol was added 5 g of magnesium turnings, on completion of reaction the methanol was refluxed for 2 h and distilled. Benzene was refluxed with metallic sodium and distilled. Acetonitrile was boiled several times till it stopped to take color and then distilled. It was kept on molecular sieves 3A.

Ethoxycarbonylmethylenetriphenylphosphonium chloride (II) [22]. A solution of 0.01 mol of triphenylphosphine and 0.11 mol of alkyl chloroacetate in 10 ml of anhydrous acetonitrile was boiled till complete consumption of triphenylphosphine (TLC monitoring). This process takes about 48 h. The solution was concentrated to a half of its volume, and ethyl acetate was added till the solution turned slightly turbid. Then the reaction mixture was left standing for 12 h to the end of crystallization. The salt was filtered off, washed with ethyl acetate, and dried in a vacuum. Yield 90%.

Phenyliodoniumethoxycarbonylmethylenetriphenylphosphorane borofluoride (I). Method 1. To 5 ml of anhydrous methanol was gradually added 0.01 mol of metallic sodium, and after its complete dissolution was gradually added dropwise a solution of 0.01 mol of phosphonium salt **II** in 5 ml of anhydrous methanol. The reaction mixture was cooled with ice water for 1 h till complete precipitation of sodium chloride. The solution of ylide **III** was filtered from the NaCl precipitate and was used directly in the next stage of the reaction. Ylide **III** solution was cooled to 0°C, and a solution of 0.01 mol of phenyliodoso acetate in 8 ml of anhydrous methanol was added controlling the addition rate so as the reaction temperature did not exceed 0°C. Then 0.01 mol of 40% solution of HBF_4 was added maintaining the temperature at 0°C. The solution was stirred at the same 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. The yield of compound **I** 40%, mp 190–191°C.

Method 2. To a solution of 5 g (0.013 mol) of ethoxycarbonylmethylenetriphenylphosphonium chloride (**II**) in 19 ml of water was added 5 ml at 80% solution of NaOH till pH 8. The separated precipitate was filtered off, washed with water, dried, and recrystallized from ethanol (15 ml), washed with ether, and dried. We obtained 3.5 g (77%) of ylide **III**, mp 112–113°C [22].

To a solution of 3.5 g (0.01 mol) of ylide **III** in 5 ml of methanol cooled to 0°C was added a solution of 3.25 g (0.01 mol) of phenyliodoso diacetate in 19 ml of methanol maintaining the temperature of the reaction mixture below 5°C. Then 2.5 ml of 40% HBF_4 solution was added maintaining the temperature of the reaction mixture within 0–5°C range. The mixture was stirred for 1 h, then 10 ml of ethyl ether was added, and the stirring continued for 1 h more. The separated precipitate was filtered off and washed with ether. We obtained 5.3 g (85%) of ylide **I**, mp 190–191°C. IR spectrum, ν , cm^{-1} : 1600, 1570, 1486. Found, %: C 52.44; H 3.89; I 20.55. $\text{C}_{28}\text{H}_{25}\text{BF}_4\text{IO}_2\text{P}$. Calculated, %: C 52.66; H 3.90; I 19.89.

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