Selective monoalkylation of phosphorus-substituted CH acids with (bromomethyl)- and 1,4-bis(bromomethyl)benzenes

I. L. Odinets, O. I. Artyushin, S. V. Lenevich, G. V. Bodrin, K. A. Lyssenko, I. V. Fedyanin, P. V. Petrovskii, and T. A. Mastryukova*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5085. E-mail: odinets@ineos.ac.ru

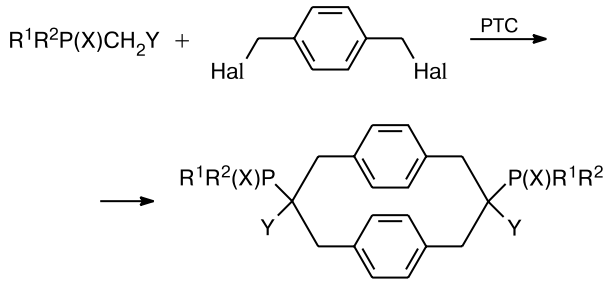
C-Alkylation of phosphorus-substituted CH acids with various substituted (bromomethyl)arenes under phase transfer catalysis conditions (K_2CO_3/MeCN) proceeds with high selectivity (75—100%) as monoalkylation.

Key words: CH acids, phosphorylacetonitriles, thiophosphorylacetonitriles, alkylation, (bromomethyl)benzene, 1,4-bis(bromomethyl)benzene, phase transfer catalysis, X-ray diffraction analysis.

C-Alkylation of various types of CH acids, including phosphorus(IV)-substituted CH acids, using various bases and heterophase systems finds wide application in preparative organic chemistry for modifying the structures of starting substrates[1,2] and is, apparently, one of the most extensively studied reactions proceeding under phase transfer catalysis (PTC) conditions. It should also be noted that alkylation of CH acids is the reaction, in which phase transfer catalysis has been discovered for the first time. These reactions proceed readily with benzyl halides possessing higher electrophilicity compared to aliphatic primary haloalkanes, due to which even their chlorine-substituted derivatives can be used,[3,4] although such examples are few in number. In particular, the reaction of dimethylamide of cyanomethylphosphonic acid with benzyl chloride in the NaOH (50%)/CH_2Cl_2 system proceeded with rather high selectivity as C-monoalkylation (71% yield).[3] C,C-Dialkylation of diethoxyphosphorylacetonitrile with benzyl chloride (46% yield) and its *para*-fluorine-substituted derivative (70% yield) was carried out under conditions of ion-pair extraction (12.5 *M* NaOH/TEBA,* 60 °C).[4] As for alkylation of phosphorus-substituted CH acids with poly(halomethyl)arenes, only exhaustive cycloalkylation of (thio)phosphorylacetonitriles with hexakis(bromomethyl)benzene in the K_2CO_3 (or Cs_2CO_3)/MeCN—DMSO system (95 : 5) was described. The latter reaction gave rise to a mixture of geometric isomers of 2,5,8-tris[diphenyl(thio)phosphoryl]-2,3,4,5,6,7,8,9-octahydro-1*H*-cyclopenta[*e*]-*as*-indacene-2,5,8-tricarbonitrile (tris-phosphorylated triindanes).[5]

It is well known that alkylation of CH acids can be directed toward either selective mono- or dialkylation by varying the type of phase transfer systems.[3,4,6] Hence, it was of interest to examine the possibility of the use of disubstituted (halomethyl)arenes, for example, 1,4-bis(bromomethyl)benzene, as synthons for the preparation of new types of functionalized macrocycles (Scheme 1). Such compounds with the exocyclic P atom attached to the macrocyclic core are of interest as chelating and extractive agents, which is able not only to be coordinated at the P=X group but also to form guest—host inclusion compounds as well as precursors of new types of phosphine ligands for metal complex catalysis.

Scheme 1



X = O, S; Y = CN, COOR, C(O)R; R^1, R^2 = OAlk, Alk, Ar

We used the phase-transfer catalyzed reaction of diphenylphosphorylacetonitrile (**1a**) with benzyl bromide (**2a**) as a model process for determining the conditions for the reaction proceeding as dialkylation. We chose substrate **1a** as the CH acid because phosphorylacetonitriles (Horner—Emmons reagents) and their thiophosphorylated analogs are readily available and are not tend to exhibit dual reactivity in PTC reactions.

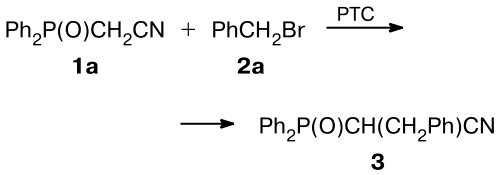
* TEBA is triethylbenzylammonium chloride.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 209—217, January, 2004.

1066-5285/04/5301-0219

It appeared that the reactions of compounds **1a** and **2a** readily proceeded at ~20 °C with the use of potassium carbonate as the base and MeCN as the organic phase to give (regardless of the ratio between the starting reagents) the corresponding monobenzyl-substituted derivative **3** in high yield (Scheme 2). An increase in the temperature (MeCN, 80 °C) leads only to a decrease in the reaction time but does not change the direction of the reaction. An analogous result was obtained with the use of an MeCN—DMSO mixture (in ratios from 9 : 1 to 8 : 2) as the organic phase.

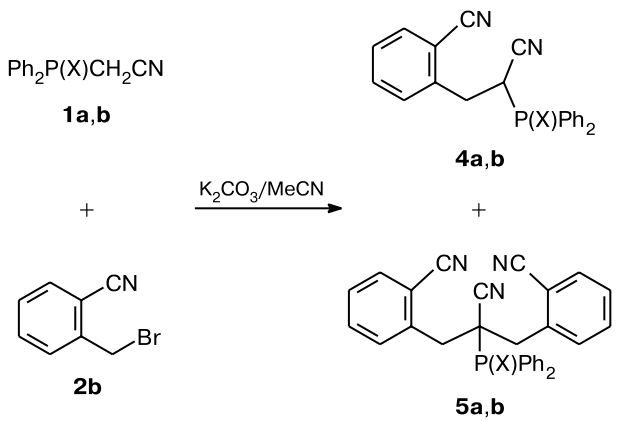
Scheme 2



It is known that the reactions of compound **1a** with α,ω-dihaloalkanes,[7] α,ψ-dihaloalkanes,[8] and hexakis(bromomethyl)benzene[5] in the K_2CO_3/DMSO system proceed as exhaustive cycloalkylation. However, in our study, the reactions afforded only 23% of the corresponding dialkylation product (according to the ^{31}P NMR spectroscopic data) even with the use of this heterophase system and an excess of benzyl bromide.

Although the reactions of diphenylphosphorylacetonitrile (**1a**) and its thiophosphoryl analog **1b** with the use of *o*-cyano-substituted (bromomethyl)benzene **2b** as an electrophilic component also proceeded predominantly as monoalkylation (the yields of compounds **4a**,**b** were higher than 75%), double alkylation products **5a**,**b** were generated (in 15—17% yields) already in a soft phase transfer system, such as K_2CO_3/MeCN (Scheme 3). The use

Scheme 3

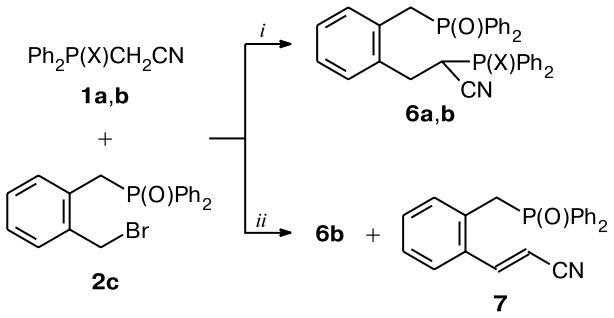


X = O (**a**), S (**b**)

of the MeCN—DMSO solvent mixture (9 : 1) led to an increase in the percentage of the double alkylation product to 25%, whereas the yields of compounds **4a**,**b**, correspondingly, decreased.

The reactions of nitriles **1a**,**b** with 2-diphenylphosphorylmethyl(bromomethyl)benzene (**2c**) in the K_2CO_3/MeCN system proceeded exclusively as monoalkylation (Scheme 4). When DMSO was used as the solvent for substrate **1a**, the direction of the reaction persisted and the overall rate of the process only slightly increased (in both systems, product **6a** was prepared in approximately equal yields). According to the ^{31}P NMR spectroscopic data, the reaction of nitrile **1b** in DMSO afforded a mixture consisting of the starting compound **1b** (36%), product **6b** (36%), and 2-propenenitrile **7** (28%). The latter product was, evidently, generated due to elimination of the diphenylthiophosphoryl fragment from **6b**. (*E*)-3-{2-[(Diphenylphosphoryl)methyl]phenyl}prop-2-enenitrile (**7**) was isolated from the reaction mixture in the individual state in low yield by fractional crystallization.

Scheme 4



X = O (**a**), S (**b**)

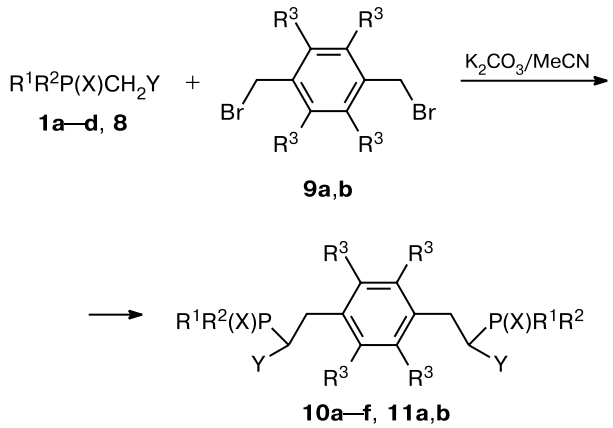
i. X = O, S; K_2CO_3/MeCN or X = O; K_2CO_3/DMSO.
ii. X = S, K_2CO_3/DMSO

Apparently, high selectivity of the reactions of phosphoryl- and thiophosphorylacetonitriles with various (bromomethyl)benzenes in the K_2CO_3/MeCN system is attributed not to steric factors or thermodynamic favorability of the monoalkylation product but to low solubility of primary C-alkylation products in MeCN, due to which they are removed from the reaction sphere. In particular, compounds **4a**,**b** produced in the reaction with 2-(bromomethyl)benzonitrile (**2b**) have the highest solubility in MeCN, and it is this reaction that proceeded with the lowest selectivity. The above assumption is supported also by a decrease in selectivity of the reaction with benzyl bromide (see Scheme 2) in the presence of DMSO as the organic phase, because product **3** is more soluble in DMSO than in MeCN. Since 2-(diphenylphosphoryl)- and 2-(diphenylthiophosphoryl)-3-{2-[(diphenylphospho-

ryl)methyl]phenyl}propanenitriles **6a**,**b** have low solubility even in DMSO, the nature of the solvent has no effect on the selectivity of their reactions. Low solubility in MeCN makes it possible to isolate easily the final solid product by filtration after the addition of water to the reaction mixture. It should be noted that this treatment often affords products as stable hydrates, which are only sometimes destroyed upon subsequent recrystallization from nonaqueous solvents.

Therefore, in attempting to perform double alkylation of phosphoryl- and thiophosphorylacetonitriles **1a**—**d** with 1,4-bis(bromomethyl)arenes **9a**,**b**, which could afford macrocycles in a substantially dilute reaction mixture, we prepared products of double monoalkylation at both bromomethyl fragments of the electrophilic component in high yields* (the reagent ratio was 2 : 1) (Scheme 5). A change in the reagent ratio has no effect on the reaction pathway and only hinders isolation of the target products.

Scheme 5



9: R^3 = H (**a**), Me (**b**)

Compound	R^1	R^2	R^3	X	Y
1a	Ph	Ph	—	O	CN
1b	Ph	Ph	—	S	CN
1c	Ph	EtO	—	O	CN
1d	EtO	EtO	—	O	CN
8	Ph	Ph	—	O	COOEt
10a	Ph	Ph	H	O	CN
10b	Ph	Ph	H	S	CN
10c	Ph	Ph	Me	O	CN
10d	Ph	Ph	Me	S	CN
10e	Ph	EtO	Me	O	CN
10f	EtO	EtO	Me	O	CN
11a	Ph	Ph	H	O	COOEt
11b	Ph	Ph	Me	O	COOEt

It should also be noted that ethyl diphenylphosphorylacetate (**8**) reacted with compounds **9a**,**b** in a similar way to give the corresponding diphosphorylated derivatives **11a**,**b**. However, in this case, the reagent ratio **8** : **9** = 1.2 : 1 appeared to be most efficient, because the phase-transfer catalyzed reaction was accompanied by partial hydrolysis of the ester fragment in ester **8** and the resulting diphenylphosphorylacetic acid did not undergo CH-alkylation.

In this case, the reaction products are also poorly soluble in MeCN. After aqueous treatment of the mixture, these products can easily be isolated by filtration as crystal hydrates of individual compounds; impurities of the unconsumed starting reagents, potassium carbonate, and small amounts of by-products (for example, hydrolysis products of ester **8**) can be removed by washing with either water or MeCN. In some cases, crystal hydrate can be decomposed and water of crystallization can be removed upon subsequent recrystallization.

The compositions and structures of all the compounds synthesized were confirmed by elemental analysis data (Table 1) and the IR and ^{1}H, ^{31}P, and ^{13}C NMR spectra (Tables 2 and 3). In addition, the structure of 2-[2-cyano-2-(diphenylphosphoryl)ethyl]benzonitrile (**4a**) was established by single-crystal X-ray diffraction analysis. The overall view of molecule **4a** is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 4. In the crystal, the cyano group in the α position with respect to the P atom (at the C(1) atom) has a synperiplanar conformation relative to the phosphoryl group; the O(1)—P(1)—C(1)—C(9) torsion angle is 68°. The P(1)—C(1)—C(2)—C(3) fragment adopts an antiperiplanar conformation (the P(1)—C(1)—C(2)—C(3) torsion angle is −172.8°). The cyano-substituted phenyl group is nearly orthogonal to the latter fragment (the C(1)—C(2)—C(3)—C(8) torsion angle is −102.5°). Hence, the conformation of molecule **4a** in the crystal excludes the formation of intramolecular contacts of the cyano substituent (C(10)N(2)) of the phenyl ring with both the α-H(1) atom and the H atoms of the $P(O)Ph_2$ group.

Analysis of the crystal packing demonstrated that the molecules are linked in chains extended along the crystallographic *c* axis *via* strong C—H...O contacts involving the H(1) atom (C(1)...O(1′), 3.151(3) Å; H(1)...O(1), 2.17 Å; C(1)—H(1)—O(1), 149°) and the H(16) atom (C(16)...O(1′), 3.390(3) Å; H(16)...O(1), 2.31 Å; C(1)—H(1)—O(1), 173°). These chains, in turn, are linked *via* C—N...H contacts (C(21)...N(2′), 3.416(3) Å; H(21)...N(2′), 2.49 Å; C(21)—H(21)—N(2′), 163°) in a layer parallel to the *bc* plane, the phenyl groups forming a hydrophobic coating of the layer (Fig. 2).

The IR spectra of compounds **3**, **6a**,**b**, and **10a**—**f** have characteristic CN stretching bands in the region of 2230—2240 cm^{-1} and CH_2 bending bands at 1437—1445 cm^{-1}. In the spectra of compounds **4a**,**b** and **5a**, each cyano group appears as an individual absorption

* The use of a 5—10 mol.% phase transfer catalyst, for example TEBA, Bu_4NHSO_4, or Bu_4NCl, appeared to be most efficient in the reacitons of thiophosphorylacetonitriles.

Table 1. Yields, melting points, elemental analysis data, and results of IR spectroscopy for compounds **3**—**7**, **10**, and **11**

Compound	Yield[a] (%)	M.p./°C (solvent)	Found / Calculated (%)			Molecular formula	IR, ν/cm^{-1}		
			C	H	N		ν(CN) (**11**: ν(C=O))	ν(P=O) (ν(P=S))	ν(CH$_2$)[b]
3	97 (83)	174—175 (hydrate); 195—196 (EtOH)	76.16 76.12	5.54 5.47	4.21 4.23	$C_{21}H_{18}NOP$	2240	1190, 1215	1437
4a	67 (54)	181 (EtOH)	74.11 74.15	4.63 4.81	8.07 7.86	$C_{22}H_{17}N_2OP$	2230, 2240	1198, 1225	1445
4b	77 (65)	133 (EtOH)	70.92 70.95	4.69 4.60	7.41 7.52	$C_{22}H_{17}N_2SP$	2232, 2240	(675)	1445
5a	17 (10)	212—213 (MeOH)	76.01 76.42	4.42 4.70	8.36 8.91	$C_{30}H_{22}N_3OP$	2235, 2240	1195, 1215	1442
6a	88 (71)	278 (MeCN—H_2O)	72.27 72.46	5.23 5.54	2.41 2.49	$C_{34}H_{29}NO_2P_2 \cdot H_2O$	2235	1187, 1190	1437
6b[c]	79 (64)	135—136 (MeCN—H_2O)	70.15 70.45	5.37 5.39	—	$C_{34}H_{29}NOP_2S \cdot H_2O$	2235	1195 (620)	1432
7[d]	27 (15)	225 (decomp.) (MeOH)	76.35 76.96	5.58 5.28	3.88 4.08	$C_{22}H_{18}NOP$	2210	1190	1442
10a	87 (74)	310 (EtOH)	70.44 70.69	4.85 4.53	4.54 4.58	$C_{36}H_{30}N_2O_2P_2 \cdot 1.5H_2O$	2240	1195	1445
10b	80 (55)	255 (CH_2Cl_2—Et_2O)	70.18 70.01	5.01 4.87	4.35 4.55	$C_{36}H_{30}N_2P_2S_2$	2230	(628)	1440
10c	100 (92)	266 (MeCN—H_2O)	73.88 73.95	5.73 6.01	4.22 4.31	$C_{40}H_{38}N_2O_2P_2 \cdot 0.5H_2O$	2237	1205, 1183	1438
10d	100 (87)	164 (CH_2Cl_2—MeCN)	70.21 70.40	5.71 5.72	3.84 4.11	$C_{40}H_{38}N_2S_2P_2 \cdot 0.5H_2O$	2237	(658)	1437
10e	100 (83)	248—249 (MeCN—H_2O)	65.74 65.67	7.01 6.71	4.58 4.71	$C_{32}H_{38}P_2O_6N_2 \cdot 0.5H_2O$	2241	1260	1443
10f	95 (86)	173—174 (CH_2Cl_2—pentane)	56.40 56.24	7.24 7.47	5.31 5.47	$C_{24}H_{38}N_2P_2O_2$	2240	1262, 1251, 1231	1440
11a[e]	92 (76)	247—248 (EtOH)	68.82 68.96	5.88 6.08	—	$C_{40}H_{40}O_6P_2 \cdot H_2O$	1722	1204, 1187, 1183	1436
11b	95 (70)	265—266 (THF)	71.37 71.92	6.61 6.58	—	$C_{44}H_{48}O_6P_2$	1720	1198, 1215	1435

[a] The yields are given according to the ^{31}P NMR spectroscopic data, the yields of the compounds isolated are given in parentheses.
[b] Bending vibrations.
[c] Found (%): P, 11.07. Calculated (%): P, 10.69.
[d] ν(C=C) = 1620 cm^{-1}.
[e] Found (%): P, 8.82. Calculated (%): P, 8.89.

band. In the spectrum of compound **7** containing the cyanovinyl fragment, the CN absorption band is shifted to longer wavelengths (2210 cm^{-1}), and the absorption band of the C=C double bond is observed at 1620 cm^{-1}. In the spectra of compounds **11** containing the carboalkoxy group, the C=O absorption band is observed in the characteristic region of 1720—1725 cm^{-1}. The P=O absorption band, whose position varies depending on the number of the P—C bonds at the P atom, often has two maxima. For compound **6a**, these bands correspond, apparently, to absorption of two different phosphoryl fragments. In the spectra of other compounds, these bands belong, presumably, to two different stereoisomers.

In spite of the fact that compounds **10** and **11** contain two asymmetric C atoms (except for compound **10e** with four asymmetric centers) and are generated as statistical mixtures of *meso* and *d*,*l* forms, the signals of the stereoisomers in the ^{31}P NMR spectra of most of the compounds in solutions in $CDCl_3$ coincide with each other, and two individual singlets are observable in the spectra measured in DMSO-d_6. Nevertheless, several sets of characteristic signals corresponding to stereoisomers are observed in some ^{13}C NMR spectra even in solutions in $CDCl_3$. It should be noted that the ^{31}P NMR spectrum of a solution (in $CDCl_3$) of compound **10e**, in which the P atoms are also asymmetric, shows two pairs of signals. The distance between the signals of isomers **10e**-**A** and **10e**-**B** is about 1 ppm, whereas the distances for the *meso* and *d*,*l* forms are as small as hundredths of ppm.

In the ^{13}C NMR spectra, the signal of the C atom bound to the P atom appears as a characteristic doublet at δ 30.3—37.3 (Y = CN) and 49.5—51.0 (Y = COOAlk,

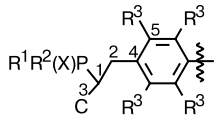
Table 2. Parameters of the $^{31}P\{^1H\}$ and ^1H NMR spectra of compounds **3**—**7**, **10**, and **11**

Compound	^{31}P NMR, δ		^1H NMR ($CDCl_3$), δ (J/Hz)
	$CDCl_3$	DMSO	
3	27.78	—	2.83 (ABX system, 1 H, H_B (CH_2), $^2J_{H,H}$ = 13.6, $^3J_{P,H}$ = 11.6, $^3J_{H,H}$ = 7.6); 3.42 (ABX system, 1 H, H_A (CH_2), $^2J_{P,H}$ = 11.6, $^3J_{H,H}$ = 7.6); 3.57 (m, 1 H, CHP(O), $^2J_{P,H}$ =16.8); 7.22—7.34, 7.43—7.68, 7.80—7.91, 7.99—8.01 (all m, 5 H + 6 H + 2 H + 2 H, Ph)
4a	27.95		3.19—3.27, 3.40—3.47 (both m, 2 H each, CH_2); 3.83 (appeared as dt, 1 H, CHCN, $^3J_{P,H}$ = $^3J_{H,H}$ = 12.4, $^3J_{H,H}$ = 4.4); 7.38 (t, 1 H, Ar, $^3J_{H,H}$ = 7.6); 7.42 (d, 1 H, Ar, $^3J_{H,H}$ = 7.6); 7.55—7.60 (m, 1 H + 4 H, Ar + *m*-H (Ph)); 7.62—7.66 (m, 1 H + 2 H, Ar + *p*-H (Ph)); 7.93—8.01 (m, 4 H, *o*-H (Ph))
4b	46.28	—	3.25 (m, 1 H, ABX system, CH_2, $^2J_{H,H}$ = 14.0, $^2J_{P,H}$ = 12.0, $^3J_{H,H}$ = 7.6); 3.35 (m, 1 H, ABX system, CH_2, $^2J_{H,H}$ = 14.0, $^2J_{P,H}$ = 10.5, $^3J_{H,H}$ = 4.6); 4.09 (appeared as dt, 1 H, CHCN, $^3J_{P,H}$ = $^3J_{H,H}$ = 12.0, $^3J_{H,H}$ = 4.6); 7.38 (t, 1 H, Ar, $^3J_{H,H}$ = 7.6); 7.47 (d, 1 H, Ar, $^3J_{H,H}$ = 7.6); 7.55—7.63 (m, 2 H + 6 H, Ar + *m*-H, *p*-H (Ph)); 8.00—8.08 (m, 4 H, *o*-H (Ph))
5a	26.08	—	3.46—3.60 (m, 4 H, $\underline{C}H_2Ar$); 7.28—7.27, 7.35—7.43, 7.49—7.55, 8.06—8.11 (all m, 6 H + 4 H + 4 H + 4 H, Ar + Ph)
5b	53.20	—	—
6a*	—	29.34, 29.90	2.92—3.02 (m, 2 H, $C\underline{H}_2CH$); 3.58 (t, 1 H, $C\underline{H}_2P(O)$, $^2J_{P,H}$ = $^2J_{H,H}$ = 15.0); 3.87 (dd, 1 H, $C\underline{H}_2P(O)$); 5.31—5.37 (m, 1 H, CH); 6.73 (d, 1 H, Ar, $^3J_{H,H}$ = 7.6); 6.97 (t, 1 H, Ar, $^3J_{H,H}$ = 7.6); 7.13 (t, 1 H, Ar, $^3J_{H,H}$ = 7.6); 7.20—7.25, 7.44—7.52, 7.60—7.69, 7.84—7.92, 7.98—8.02 (all m, 21 H, 3 H + 3 H + 9 H + 4 H + 2 H, Ar + Ph)
6b*	—	48.74 (P=S), 29.88 (P=O)	2.86—2.89, 2.96—3.00 (both m, 1 H each, $C\underline{H}_2CH$); 3.57, 3.88 (both t, 1 H each, $CH_2P(O)$, $^2J_{P,H}$ = $^2J_{H,H}$ = 14.8); 5.78—5.82 (m, 1 H, CH); 6.72 (d, 1 H, Ar, $^3J_{H,H}$ = 7.4); 6.97 (t, 1 H, Ar, $^3J_{H,H}$ = 7.4); 7.40 (t, 1 H, Ar, $^3J_{H,H}$ = 7.4); 7.10—7.22, 7.51—7.71, 7.85—7.89, 7.99—8.05, 8.15—8.20 (all m, 21 H, 3 H + 3 H + 9 H + 4 H + 2 H, Ar + Ph)
7	28.92	—	3.71 (d, 2 H, $CH_2P(O)$, $^2J_{P,H}$ = 13.6); 5.52 (d, 1 H, CH=); 7.17 (d, 1 H, Ar, $^3J_{H,H}$ = 7.6); 7.25 (t, 1 H, Ar, $^3J_{H,H}$ = 7.4); 7.35 (d, 1 H, Ar, $^3J_{H,H}$ = 7.6); 7.44—7.50, 7.52—7.59, 7.64—7.73 (all m, 12 H, CH= + Ar + Ph)
10a	27.77	29.57, 29.55	2.75—2.85, 3.33—3.41 (both m, 2 H each, CH_2); 3.49—3.58 (m, 2 H, CHCN); 7.18 (s, 4 H, C_6H_4); 7.50—8.05 (m, 20 H, 4 Ph)
10b	45.60	48.32	2.87—2.95, 3.40—3.48 (both m, 2 H each, CH_2); 3.66—3.77 (m, 2 H, CHCN); 7.35 (s, 4 H, C_6H_4); 7.60—7.71 (m, 12 H, *m*-H, *p*-H (Ph)); 7.97, 8.16 (both dd, 4 H each, *o*-H (Ph), $^3J_{P,H}$ = 13.6, $^3J_{H,H}$ = 7.2)
10c	28.19, 28.11	29.81, 29.69	2.13 (s, 12 H, Me); 3.15—3.25, 3.32—3.35 (both m, 2 H each, CH_2); 3.45—3.55 (m, 2 H, CH); 7.50—7.69 (m, 12 H, *m*-H, *p*-H (Ph)); 7.85—7.92, 8.05—8.12 (both m, 8 H, *o*-H (Ph))
10d	45.88	49.52, 49.50	2.10 (s, 12 H, Me); 3.15—3.35 (m, 4 H, CH_2); 3.52—3.68 (m, 2 H, CH); 7.48—7.65 (m, 12 H, *m*-H, *p*-H (Ph)); 7.85—7.90, 8.12—8.17 (both m, 4 H each, *o*-H (Ph))
10e-A**	34.10, 34.13	34.13	1.37—1.44 (t, 6 H, $C\underline{H}_3CH_2$, $^3J_{H,H}$ = 6.8); 2.10 (**A**), 2.15 (**B**) (s, 12 H, $C\underline{H}_3Ar$); 2.92—3.10 (m, 2 H, $C\underline{H}_2CH$); 3.18—3.24 (m, 3 H, $C\underline{H}_2CH$ + CH); 3.36—3.48 (m, 1 H, CH); 4.09—4.21
10e-B**	33.09, 33.12	33.12	(**A**), 4.21—4.37 (**B**) (m, 4 H, OCH_2); 7.54—7.70 (m, 6 H, *m*-H, *p*-H (Ph)); 7.89—8.00 (m, 4 H, *o*-H (Ph))
10f	18.09	20.05	1.39 (t, 6 H, $C\underline{H}_3CH_2$, $^3J_{H,H}$ = 6.8); 1.40 (t, 6 H, $C\underline{H}_3CH_2$, $^3J_{H,H}$ = 7.2); 2.27 (s, 12 H, $C\underline{H}_3Ar$); 3.03 (ABX system, 2 H_A, $C\underline{H}_2Ar$, $^2J_{H,H}$ = 12.0, $^2J_{P,H}$ = 23.2, $^3J_{H,H}$ = 4.0); 3.20—3.28 (m, 2 H_B, $C\underline{H}_2Ar$); 3.37—3.46 (m, 2 H, CH); 4.22—4.36 (m, 8 H, $OC\underline{H}_2CH_3$)
11a	29.42	26.95 (br.)	0.76 (t, 6 H, $C\underline{H}_3CH_2$, $^3J_{H,H}$ = 6.8); 3.06 (ABX system, 2 H_A, $C\underline{H}_2Ar$, $^2J_{H,H}$ = 14.1, $^2J_{P,H}$ = 9.4, $^3J_{H,H}$ = 2.9); 3.20—3.28 (m, 2 H_B, $C\underline{H}_2Ar$); 3.65—3.80 (m, 6 H, $OC\underline{H}_2$ + CH); 6.97 (s, 4 H, C_6H_4); 7.44—7.54, 7.81—7.90 (both m, 12 H + 8 H, 4 Ph)
11b	29.82, 29.67	—	0.71 (t, 6 H, $C\underline{H}_3CH_2$, $^3J_{H,H}$ = 7.2); 2.00 (s, 12 H, $C\underline{H}_3Ar$); 3.13—3.19 (m, 2 H, $C\underline{H}_2CH$); 3.46—4.02 (m, 8 H, $C\underline{H}_2CH$ + OCH_2 + CH); 7.43—7.53, 7.78—7.83, 7.94—8.00 (all m, 12 H + 4 H + 4 H, 4 Ph)

* The ^1H NMR spectrum was recorded in DMSO-d_6.

** In the ^1H NMR spectrum, most of the signals for the isomers **A** and **B** overlap with each other.

Table 3. Parameters of the ^{13}C NMR spectra (δ, *J*/Hz) of compounds **3**, **4a**,**b**, **10a**,**c**,**d**,**e**,**f**, and **11a**,**b**



Compound	C(2) (d)	C(1) (d)	C(3) (d)	C(4) (d)	C_{Ar} (s)	R^1R^2 [a]	R^3
3	31.80	35.98 ($^1J_{P,C}$ = 61.1)	117.03	136.25 ($^3J_{P,C}$ = 10.8)	127.44, 129.045	128.89, 129.01 (both d, *m*-C (Ph), $^3J_{P,C}$ = 12.4); 130.17 (d, P—C, $^1J_{P,C}$ = 93.1); 131.18 (d, P—C, $^1J_{P,C}$ = 93.3); 131.14 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.6); 131.94 (d, *o*-C (Ph), $^2J_{P,C}$ = 8.4); 133.04, 136.25 (both s, *p*-C (Ph))	—
4a	30.45	34.54 ($^1J_{P,C}$ = 59.8)	115.57 ($^2J_{P,C}$ = 5.2)	139.63 ($^3J_{P,C}$ = 11.2)	128.17, 130.74, 133.02, 133.23	128.25 (d, P—C_{Ar}, $^1J_{P,C}$ = 104.0); 129.67 (d, P—C, $^1J_{P,C}$ = 106.0); 128.93 (d, *m*-C (Ph), $^3J_{P,C}$ = 12.8); 129.08 (d, *m*-C (Ph), $^3J_{P,C}$ = 12.4); 131.17 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.6); 131.40 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.2); 133.10 (s, *p*-C (Ph))	117.17 [b]
4b	31.42	37.30 ($^1J_{P,C}$ = 46.6)	115.59 ($^2J_{P,C}$ = 5.6)	139.64 ($^3J_{P,C}$ = 12.8)	128.26, 131.17, 133.10, 133.30	128.16 (d, P—C_{Ar}, $^1J_{P,C}$ = 66.2); 128.98 (d, P—C, $^1J_{P,C}$ = 65.8); 128.11 (d, *m*-C (Ph), $^3J_{P,C}$ = 12.8); 128.88 (d, *m*-C (Ph), $^3J_{P,C}$ = 12.4); 131.65 (d, *o*-C (Ph), $^2J_{P,C}$ = 10.4); 131.75 (d, *o*-C (Ph), $^2J_{P,C}$ = 10.8); 132.72, 132.74 (both s, *p*-C (Ph))	117.36 [b]
10a	31.48 ($^2J_{P,C}$ = 5.6); 31.42 ($^2J_{P,C}$ = 5.6)	36.01 ($^1J_{P,C}$ = 61.0); 35.79 ($^1J_{P,C}$ = 60.7)	116.96 ($^2J_{P,C}$ = 3.0); 116.98 ($^2J_{P,C}$ = 2.2)	135.77 ($^3J_{P,C}$ = 11.1); 135.79 ($^3J_{P,C}$ = 11.1)	129.29, 129.35	128.89 (d, *m*-C (Ph), $^3J_{P,C}$ = 12.4); 129.02 (d, *m*-C (Ph), $^3J_{P,C}$ = 13.4); 131.13 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.5); 131.93 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.1); 132.94, 133.08 (both s, *p*-C (Ph))	—
10c	25.8 ($^2J_{P,C}$ = 5.2)	33.43 ($^1J_{P,C}$ = 60.3)	116.99 ($^2J_{P,C}$ = 3.4); 116.96 ($^2J_{P,C}$ = 3.4)	132.27 ($^3J_{P,C}$ = 10.3)	133.44	128.88 (d, *m*-C (Ph), $^3J_{P,C}$ = 12.3); 129.80 (d, P—C, $^1J_{P,C}$ = 100.1); 131.14 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.6); 131.93 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.0); 132.94, 133.08 (both s, *p*-C (Ph))	16.88
10d	26.65 ($^2J_{P,C}$ = 5.4)	35.95 ($^1J_{P,C}$ = 45.4)	116.70 ($^2J_{P,C}$ = 5.9); 116.64 ($^2J_{P,C}$ = 5.9)	131.90 ($^3J_{P,C}$ = 12.4); 131.83 ($^3J_{P,C}$ = 12.3)	133.56 (br)	127.93 (d, P—C, $^1J_{P,C}$ = 81.4); 127.90 (d, P—C, $^1J_{P,C}$ = 81.2); 128.81 (d, *m*-C (Ph), $^3J_{P,C}$ = 12.6); 128.91, 128.93 (both d, *m*-C (Ph), $^3J_{P,C}$ = 12.7); 130.12, 130.15 (both d, P—C, $^1J_{P,C}$ = 83.7); 131.24 (d, *o*-C (Ph), $^2J_{P,C}$ = 10.4); 132.36 (d, *o*-C (Ph), $^2J_{P,C}$ = 10.1); 132.45, 132.48, 132.77, 132.80 (all *p*-C (Ph))	16.15
10e-A	26.88 ($^2J_{P,C}$ = 3.8); 26.92 ($^2J_{P,C}$ = 3.4)	30.28 ($^1J_{P,C}$ = 138.9); 30.25 ($^1J_{P,C}$ = 139.0)	115.59 ($^2J_{P,C}$ = 9.0); 115.63 ($^2J_{P,C}$ = 8.9)	128.81 ($^3J_{P,C}$ = 13.2)	133.15, 134.54 (br)	16.35 (d, $\underline{C}H_3CH_2O$, $^3J_{P,C}$ = 4.5); 63.64 (d, $CH_3\underline{C}H_2O$, $^2J_{P,C}$ = 6.8); 64.06 (d, $CH_3\underline{C}H_2O$, $^2J_{P,C}$ = 7.0); 126.24 (d, P—C_{Ph}, $^1J_{P,C}$ = 100.6); 127.56 (d, P—C_{Ph}, $^1J_{P,C}$ = 96.4); 132.22 (d, *m*-C (Ph), $^3J_{P,C}$ = 11.1); 132.24 (d, *m*-C (Ph), $^3J_{P,C}$ = 11.6); 132.27 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.7); 132.53 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.8); 133.24, 133.26 (both s, *p*-C (Ph)	16.81 (br)
10e-B	26.11 ($^2J_{P,C}$ = 3.5)	33.04 ($^1J_{P,C}$ = 91.1); 33.62 ($^1J_{P,C}$ = 91.1)	116.18 ($^2J_{P,C}$ = 9.2); 116.22 ($^2J_{P,C}$ = 8.4)	128.77 ($^3J_{P,C}$ = 13.2)	133.53 (*J* = 2.8); 133.42 (*J* = 2.0)	16.36 (d, $\underline{C}H_3CH_2O$, $^3J_{P,C}$ = 4.4); 16.39 (d, $CH_3\underline{C}H_2O$, $^3J_{P,C}$ = 4.8); 62.38 (d, $CH_3\underline{C}H_2O$, $^2J_{P,C}$ = 6.5); 62.50 (d, $CH_3\underline{C}H_2O$, $^2J_{P,C}$ = 6.4); 126.23 (d, P—C_{Ph}, $^1J_{P,C}$ = 98.6); 127.54 (d, P—C_{Ph}, $^1J_{P,C}$ = 95.4); 131.98 (d, *m*-C (Ph), $^3J_{P,C}$ = 11.3); 132.24 (d, *m*-C (Ph), $^3J_{P,C}$ = 11.2); 133.54, 133.56 (both s, *p*-C (Ph))	16.64 (br)

(*to be continued*)

Table 3 (*continued*)

Compound	C(2) (d)	C(1) (d)	C(3) (d)	C(4) (d)	C_{Ar} (s)	R^1R^2 [a]	R^3
10f	27.01 ($^2J_{P,C}$ = 3.0)	30.33 ($^1J_{P,C}$ = 138.2)	115.63 ($^2J_{P,C}$ = 9.1)	132.29 ($^3J_{P,C}$ = 13.3)	133.33	16.22, 16.24 (both d, $\underline{C}H_3CH_2OP$, $^3J_{P,C} \approx 1$); 63.69 (d, CH_2OP, $^2J_{P,C}$ = 6.7); 64.12 (d, CH_2OP, $^2J_{P,C}$ = 6.8)	16.86
11a [c]	31.51	50.97 ($^1J_{P,C}$ = 56.8)	168.63 ($^2J_{P,C}$ = 2.0)	136.90 ($^3J_{P,C}$ = 13.4)	128.50	128.19 (d, *m*-C (Ph), $^3J_{P,C}$ = 12.1); 128.47 (d, *m*-C (Ph), $^3J_{P,C}$ = 11.6); 130.17 (d, P—C, $^1J_{P,C}$ = 93.1); 131.18 (d, P—C, $^1J_{P,C}$ = 93.3); 131.00 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.2); 131.40 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.3); 131.96, 131.98 (both s, *p*-C (Ph))	—
11b [d]	26.67	49.63 ($^1J_{P,C}$ = 57.8); 49.54 ($^1J_{P,C}$ = 59.35)	169.31	133.29 ($^3J_{P,C}$ = 11.2)	132.81	128.27 (d, *m*-C (Ph), $^3J_{P,C}$ = 11.9); 128.33 (d, *m*-C (Ph), $^3J_{P,C}$ = 11.8); 130.19 (d, P—C, $^1J_{P,C}$ = 102.5); 131.20 (d, P—C, $^1J_{P,C}$ = 101.6); 131.10 (d, *o*-C (Ph), $^2J_{P,C}$ = 8.9); 131.50 (d, *o*-C (Ph), $^2J_{P,C}$ = 9.2); 131.90, 132.01 (both br.s, *p*-C (Ph))	16.73

[a] In the JMODECHO NMR spectrum, the signals of the quaternary C atoms of the Ph—P fragment are not always observable due to low solubility of hydrates of these compounds.
[b] R^3 = 2-CN.
[c] C(3)(O)O$\underline{R}$: 13.31 (Me), 60.90 (OCH_2).
[d] C(3)(O)OR: 13.24 (Me), 60.89 (OCH_2).

11a,**b**). In the spectra of compounds **10c**—**e**, which differ only in the nearest environment about the P atom, the spin-spin coupling constant $^1J_{P,C}$ changes in going from the compounds bearing the P=O group to their thiophosphoryl analogs as well as with increasing number of P—C bonds in the molecule (*i.e.*, in going from phosphonates to phosphinates and then to phosphine oxides). Interestingly, the constant $^1J_{P,C}$ for the methine C atom is substantially smaller than $^1J_{P,C}$ for the C atoms in the substituents R^1 and R^2 directly bound to the P atoms. The signals of the methylene C atom are observed as a singlet (**3**, **4a**,**b**, and **11a**) or a doublet with $^2J_{P,C} \approx 3.0$—5.6 Hz. In most cases, the signals for the stereoisomers are identical in both the position and spin-spin constant. It should

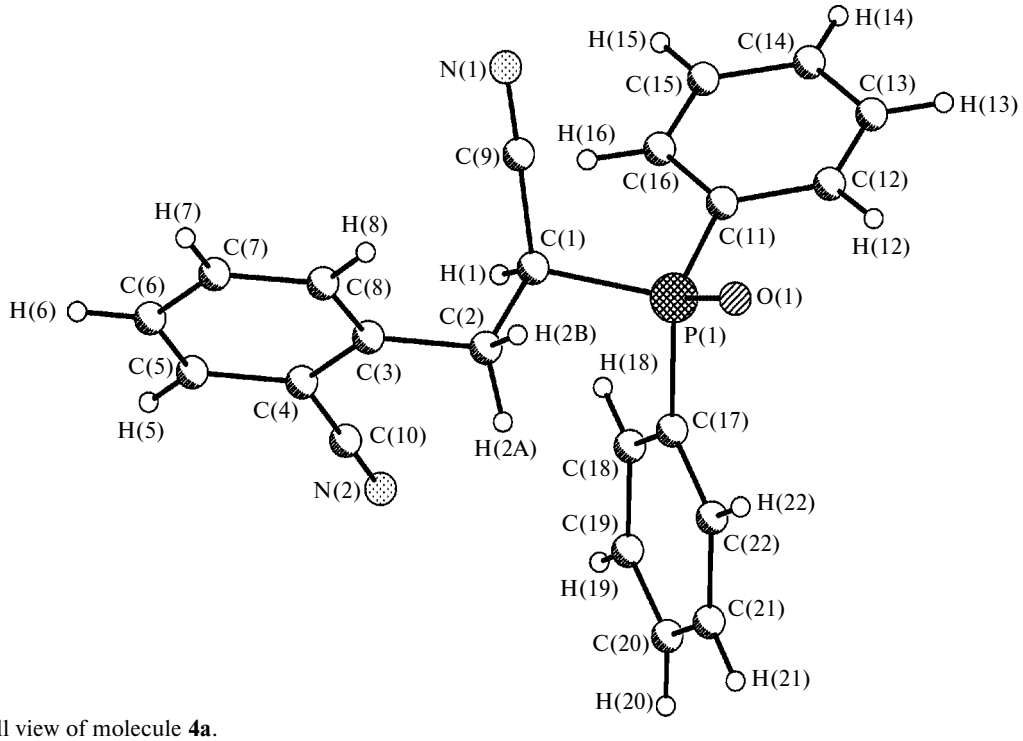


Fig. 1. Overall view of molecule **4a**.

Table 4. Selected bond lengths (*d*) and bond angles (ω) in molecule **4a**

Bond	*d*/Å	Angle	ω/deg
P(1)—O(1)	1.469(1)	O(1)—P(1)—C(1)	113.70(9)
P(1)—C(1)	1.842(2)	O(1)—P(1)—C(11)	113.40(9)
P(1)—C(11)	1.790(2)	O(1)—P(1)—C(17)	111.9(1)
P(1)—C(17)	1.802(2)	C(11)—P(1)—C(1)	107.23(9)
N(1)—C(9)	1.134(3)	C(17)—P(1)—C(1)	102.92(9)
N(2)—C(10)	1.137(3)	C(11)—P(1)—C(17)	107.00(9)
C(1)—C(9)	1.470(3)	C(9)—C(1)—C(2)	110.8(2)
C(4)—C(10)	1.429(3)	C(9)—C(1)—P(1)	110.5(1)
		C(2)—C(1)—P(1)	110.2(1)
		N(1)—C(9)—C(1)	178.5(2)
		N(2)—C(10)—C(4)	178.7(3)

also be noted that in the compounds containing two Ph substituents at the P atom, these phenyl rings are generally magnetically nonequivalent and each ring is characterized by its own set of signals of the corresponding C atoms. The spectrum of compound **10e** containing four asymmetric centers is substantially complicated.

The ^{1}H NMR spectra of the compounds under study are consistent with the above-described structures, the protons of the methylene unit always being magnetically nonequivalent. The presence of stereoisomers generally leads to complication of the characteristics pattern of an ABX system, and the corresponding spin-spin coupling constants can be estimated only in some cases.

To summarize, C-alkylation of phosphorus-containing CH acids with various substituted (bromomethyl)arenes using PTC (K_2CO_3/MeCN) proceeds selectively as monoalkylation. The selectivity decreases as the solubility of the reaction product increases, for example, in the reactions of compound **2b** with phosphoryl- and thiophosphorylacetonitriles in MeCN or with the use of DMSO as a co-solvent.

Experimental

The NMR spectra were recorded on Bruker WP-200SY and Bruker AMX-400 instruments in $CDCl_3$ and C_6D_6 using the residual signals of protons of the deuterated solvent as the internal standard (^{1}H and ^{13}C) or 85% H_3PO_4 as the external standard (^{31}P). The ^{13}C NMR spectra were measured using JMODECHO; the signals of the C atoms bearing odd and even numbers of protons have opposite polarities. The IR spectra were recorded on a Magna-IR750 (Nicolet) Fourier-transform spectrometer (spectral resolution was 2 cm^{-1}; 128 scans) in KBr pellets.

The starting phosphorylacetonitriles were prepared by the Arbuzov rearrangement of the corresponding esters of trivalent phosphorus acids under the action of chloroacetonitrile according to a known procedure.[9] The corresponding thiophosphorylacetonitriles were synthesized by the reactions of phosphoryl derivatives with Lawesson's reagent.[9] 2-(Bromomethyl)benzonitrile (**2b**) was synthesized according to a known procedure; its

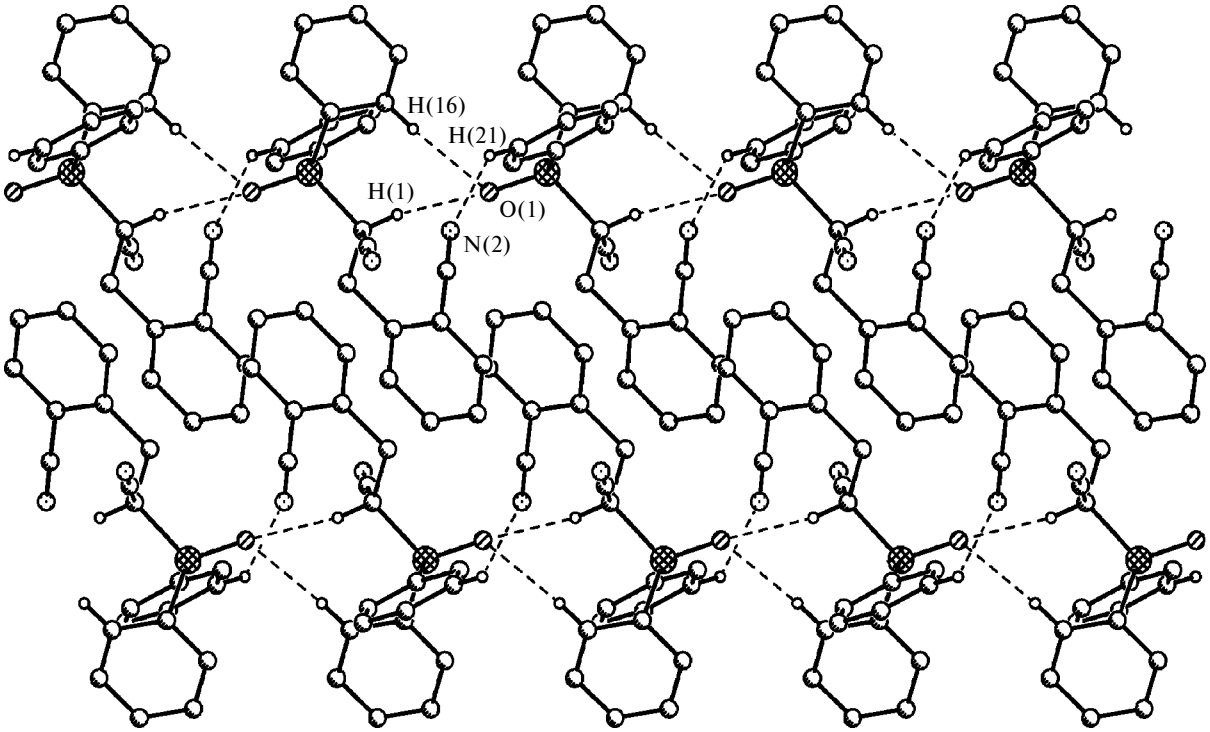


Fig. 2. Fragment of the crystal packing of compound **4a** illustrating a C—H...O- and C—H...N-bonded layer projected perpendicular to the plane of the layer.

physicochemical characteristics are identical with those published in the literature.[10]

2-Methylbenzyl(diphenyl)phosphine oxide. A mixture of 1-(bromomethyl)-2-methylbenzene (17.7 g, 0.095 mol) and ethyl diphenylphosphinite (23.0 g, 0.1 mol) in xylene (25 mL) was heated at 136—140 °C for 1 h. The reaction mixture was concentrated to one-half of the initial volume and the hot residue was diluted with an excess of hexane. The precipitate that formed was filtered off, recrystallized from benzene, washed on a filter with pentane, and dried *in vacuo* to prepare the target phosphine oxide in a yield of 27.2 g (93.0%), m.p. 142—143 °C. Found (%): C, 78.60; H, 6.30; P, 10.10. $C_{20}H_{19}OP$. Calculated (%): C, 78.42; H, 6.25; P, 10.11. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 30.02. ^1H NMR ($CDCl_3$), δ: 2.13 (s, 3 H, Me); 3.65 (d, 2 H, PCH_2, $^2J_{P,H}$ = 14.0 Hz); 6.92—7.00 (m, 2 H, Ar); 7.07—7.10 (m, 2 H, Ar); 7.40—7.45 (m, 4 H, *m*-H (PPh)); 7.48—7.53 (m, 2 H; *p*-H (PPh)); 7.64—7.73 (m, 4 H, *o*-H (PPh)).

2-(Bromomethyl)benzyl(diphenyl)phosphine oxide (2c). *N*-Bromosuccinimide (7.9 g, 0.044 mol) and a catalytic amount of a mixture of benzoyl peroxide and AIBN were added with stirring to a solution of 2-methylbenzyl(diphenyl)phosphine oxide (see above) (12.5 g, 0.041 mol) in CCl_4 (200 mL) on irradiation with a tungsten lamp. The reaction mixture was refluxed for 1 h. The resulting solid compound was filtered off and washed with warm CCl_4 (2×40 mL). The precipitate on a filter was additionally thoroughly washed with hot water (~200 mL), dried in air, and recrystallized from a benzene—EtOH mixture. An additional portion of the precipitate that formed upon concentration of the filtrate was recrystallized from the same solvent mixture. The total yield of the target product was 11.2 g (71.2%), m.p. 200—202 °C. Found (%): C, 62.70; H, 4.73; Br, 20.73; P, 8.07. $C_{20}H_{18}BrOP$. Calculated (%): C, 62.36; H, 4.71; Br, 20.74; P, 8.04. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 29.89. ^1H NMR ($CDCl_3$), δ: 3.85 (d, 2 H, PCH_2, $^2J_{P,H}$ = 13.2 Hz); 4.65 (s, 2 H, CH_2Br); 6.77 (d, 1 H, Ar, $^3J_{H,H}$ = 7.6 Hz); 7.03 (t, 1 H, Ar, $^3J_{H,H}$ = 7.6 Hz); 7.15 (t, 1 H, Ar, $^3J_{H,H}$ = 7.6 Hz); 7.30 (d, 1 H, Ar, $^3J_{H,H}$ = 7.6 Hz); 7.43—7.48 (m, 4 H, *m*-H (PPh)); 7.52—7.55 (m, 2 H, *p*-H (PPh)); 7.69 (dd, 4 H, *o*-H (PPh), $^3J_{H,H}$ = 7.6 Hz, $^3J_{P,H}$ = 11.6 Hz).

Monoalkylation of phosphoryl- and thiophosphorylacetonitriles with (bromomethyl)benzenes (general procedure). A mixture of the corresponding phosphoryl- or thiophosphorylacetonitrile **1** (1 equiv., 4.15 mmol), K_2CO_3 (4 equiv., 2.30 g, 16.60 mmol), and benzyl bromide **2** (1 equiv., 4.15 mmol) or bis(bromomethyl)arene **9a**,**b** (0.5 equiv., 2.07 mmol) in MeCN was stirred at ~20 °C for 18—20 h. The course of the reaction was monitored by ^{31}P NMR spectroscopy. Then the reaction mixture was concentrated to one-half of the initial volume and diluted with a twofold volume of water. For compounds **4a**,**b** and **11b**, the organic layer was separated and the aqueous layer was twice extracted with CH_2Cl_2. The combined extracts were dried with Na_2SO_4 and filtered. The filtrate was concentrated to dryness and the residue was recrystallized from EtOH (**4a**,**b**) or its mixture with THF (**11b**). The first portion of crystals after recrystallization of the crude mixture, which was prepared by the reactions of **1a** with **2b**, from MeOH presented dialkylated product **5a**. Its yield and physicochemical parameters are given in Table 1. In the case of compounds **3**, **6a**,**b**, **10a**—**f**, and **11a**, the reaction product that precipitated upon aqueous treatment was filtered off and dried in air. According to the ^1H and ^{31}P NMR spectroscopic data, the purity of the crude product was >95%. Generally, the crude products contained water of crystallization. Analytically pure samples were prepared by recrystallization.

X-ray diffraction study of compound 4a ($C_{22}H_{17}N_2OP$, M = 356.35). At 298 K, crystals are monoclinic, space group *C*2/*c*, *a* = 34.222(4) Å, *b* = 9.875(1) Å, *c* = 11.324(1) Å, β = 95.214(2)°, *V* = 3810.9(7) Å^3, μ = 1.56 cm^{-1}, *Z* = 8 (*Z*′ = 1), d_{calc} = 1.242 g cm^{-3}. The intensities of 11780 reflections were measured on an automated Smart 1000 CCD diffractometer at 298 K (λMo-Kα radiation, graphite monochromator, ω scanning technique, $2\theta_{max}$ = 55°), and 4376 independent reflections (R_{int} = 0.0297) were used in calculations. The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2 in the anisotropic-isotropic approximation using the SHELXTL PLUS program package. The H atoms were revealed from difference electron density syntheses and refined using the riding model. The final reliability factors were as follows: wR_2 = 0.1237, GOF = 1.097 based on all reflections (R_1 = 0.0543 was calculated using 3046 reflections with $I > 2\sigma(I)$).

This study was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-33073) and the Grant from the President of the Russian Federation (the Program "Leading Scientific Schools," Project No. NSh-1100.2003.3).

References

1. E. V. Dehmlow and S. S. Dehmlow, *Phase Transfer Catalysis*, 2nd Ed., Verlag Chemie, Weinheim, 1985.
2. M. I. Kabachnik and T. A. Mastryukova, *Mezhfaznyi kataliz v fosfororganicheskoi khimii* [*Phase Transfer Catalysis in Organophosphorus Chemistry*], URSS, Moscow, 2002, 319 pp. (in Russian).
3. J. Blanchard, N. Collognon, Ph. Savignac, and N. Normant, *Synthesis*, 1975, 655.
4. R. K. Singh, *Synthesis*, 1986, 762.
5. I. L. Odinets, O. I. Artyushin, G. V. Bodrin, P. V. Petrovskii, and T. A. Mastryukova, *Mendeleev Commun.*, 2002, **12**, 135.
6. I. L. Odinets, N. M. Vinogradova, O. I. Artyushin, R. M. Kalyanova, K. A. Lyssenko, P. V. Petrovskii, T. A. Mastryukova, and M. I. Kabachnik, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 990 [*Russ. Chem. Bull.*, 1998, **47**, 960 (Engl. Transl.)].
7. P. V. Kazakov, I. L. Odinets, A. P. Laretina, T. M. Shcherbina, P. V. Petrovskii, L. V. Kovalenko, and T. A. Mastryukova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1873 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1702 (Engl. Transl.)].
8. N. M. Vinogradova, I. L. Odinets, K. A. Lyssenko, A. A. Korlyukov, P. V. Petrovskii, G.-V. Roeschenthaler, and T. A. Mastryukova, *Mendeleev Commun.*, 2002, **12**, 133.
9. I. L. Odinets, O. I. Artyushin, P. V. Petrovskii, K. A. Lyssenko, M. Yu. Antipin, and T. A. Mastryukova, *Zh. Obshch. Khim.*, 1996, **66**, 44 [*J. Gen. Chem. USSR*, 1996, **66** (Engl. Transl.)].
10. R. C. Fuson, *J. Am. Chem. Soc.*, 1926, **48**, 833.

Received July 24, 2003;
in revised form October 21, 2003