# Reactions of phosphoryl- and thiophosphorylacetonitriles with poly(bromomethyl)arenes containing closely-spaced bromomethyl groups. New types of phosphorus-substituted fused systems

*I. L. Odinets,* O. I. Artyushin, G. V. Bodrin, M. P. Passechnik, 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*

Reactions of phosphoryl- and thiophosphorylacetonitriles with poly(bromomethyl)arenes containing closely-spaced bromomethyl groups under conditions of phase-transfer catalysis occur as cycloalkylation to form new types of fused systems, in which aromatic rings are annelated with a five-, six-, or seven-membered ring containing the exocyclic phosphorus-containing and cyano substituents. The reaction pathway is independent of the reagent ratio. Under the same conditions, the reaction with 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene affords products of monoalkylation at all electrophilic groups of the starting substrate. In the resulting compounds, the alkoxy groups at the phosphorus atom are easily transformed into the hydroxy groups *via* the corresponding silyl ethers to give the corresponding phosphorus acids, whereas the cyano group is chemically inert.

**Key words:** phosphorylacetonitriles, thiophosphorylacetonitriles, bis(bromomethyl)arenes, phase-transfer catalysis, cycloalkylation, 2-indanecarbonitriles, cyclopentanaphthalene-2-carbonitriles, indacene-2,6-dicarbonitriles, phenalene-2-carbonitriles, NMR spectra, X-ray diffraction analysis, CH-acids.

In studies of alkylation of CH-acids, most attention is generally given to three main aspects, such as the possibility of selectively preparing either mono- or dialkylation products of X—$CH_2$—Y acids, the question about the direction of alkylation in the presence of two non-equivalent acidic CH groups, and the problem of C- and O-alkylation in the presence of the carboxyalkyl or ketone group in the molecule. In these reactions, phase-transfer catalysis often allows one to control the selectivity of the reaction and to prepare the target compounds in high yields, the use of absolute media being not strictly important.[1] Examples of the use of phase-transfer catalysis in organophosphorus chemistry and, in particular, in CH-alkylation, have been described in sufficient detail in the monograph.[2]

Earlier, we have demonstrated[3] that the reactions of thiophosphorylacetonitriles with haloalkanes can be selectively performed as either C-mono- or C,C-dialkylation by varying the type of the phase-transfer catalysis system. The reactions with unsymmetrical α-bromo-ω-chloroalkanes occur at the most reactive electrophilic center, due to which both mono- and bis(ω-haloalkyl)-substituted thiophosphorylacetonitriles can be prepared. The latter were used to synthesize 3-cyano-1,2-thiaphosphacyclanes.[4,5] Cycloalkylation of esters and nitriles of (thio)phosphorylacetic acids with symmetrical α,ω- and α,ψ-dihaloalkanes has been well studied.[6—9] Alkylation of phosphorus-substituted CH-acids with benzyl halides has been less well studied. Prior to our studies, monoalkylation of cyanomethylphosphonic acid dimethylamide with benzyl chloride (50% NaOH—$CH_2Cl_2$), which occurs with rather high selectivity,[10] and dialkylation of diethoxyphosphorylacetonitrile with benzyl chloride and its *p*-fluorine-substituted derivative by ion-pair extraction (12.5 *M* NaOH/TEBA, 60 °C)[11] have been described.

Recently, we have demonstrated that CH-alkylation of phosphoryl(alkyl)acetates and (thio)phosphorylacetonitriles with (bromomethyl)arenes and 1,4-bis(bromomethyl)arenes by phase-transfer catalysis occurs selectively as monoalkylation or double monoalkylation.[12] By contrast, the reaction of (thio)phosphorylacetonitriles with hexakis(bromomethyl)benzene affords a mixture of geometric isomers of 2,5,8-tris(diphenyl(thio)phosphoryl)-2,3,4,5,6,7,8,9-octahydro-1*H*-cyclopent[*e*]-as-indacene-2,5,8-tricarbonitriles (tris-phosphorylated triindanes).[13]

To gain a complete understanding of alkylation of phosphorus-containing CH-acids with bromomethylarenes under conditions of phase-transfer catalysis, we studied this reaction with a series of bis(bromomethyl)-substituted arenes containing closely-spaced reactive elec-

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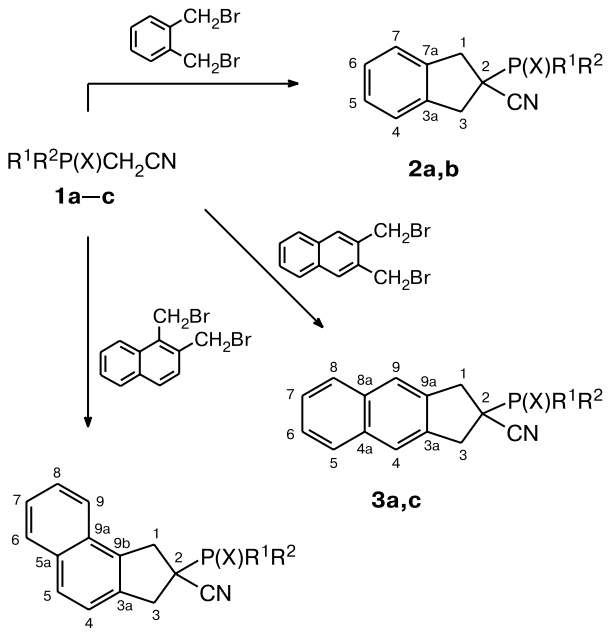
trophilic substituents. We used readily accessible phosphoryl- and thiophosphorylacetonitriles **1a—d** containing various substituents at the phosphorus atom as the starting organophosphorus substrates.

It was found that, unlike the above-described reaction with 1,4-bis(bromomethyl)arenes, alkylation of the same CH-acids with 1,2-bis(bromomethyl)benzene does not stop at the monoalkylation step but occurs as exhaustive cycloalkylation to form the annelated cyclopentane ring, 2-phosphorus-substituted 2-indanecarbonitriles **2a,b** being virtually the only reaction products regardless of the reagent ratio used. Moreover, the monitoring of the reaction by $^{31}P$ NMR spectroscopy did not reveal monoalkylation products in the reaction mixtures, *i.e.*, the rate of the second step resulting in the saturated ring closure, is much higher than the rate of the initial step. It should be noted that we have observed this fact earlier[6,8,9] in cycloalkylation of nitriles and esters of (thio)phosphorylacetic acids with α,ω-dihaloalkanes (Scheme 1).

**Scheme 1**

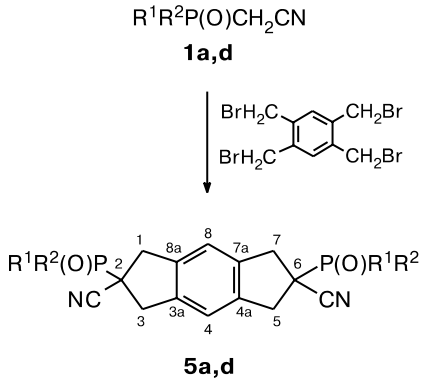



$R^1 = R^2$ = Ph, X = O (**a**); $R^1 = R^2$ = Ph, X = S (**b**);
$R^1 = R^2$ = OEt, X = O (**c**)

Extension of cycloalkylation to naphthalene derivatives containing the *o*-bromomethyl substituents in one of the fused benzene rings allowed us to synthesize the corresponding 2-(thio)phosphoryl-substituted 2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene-2-carbonitriles (**3a,c**) and 2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-2-carbonitriles (**4a,b**) (see Scheme 1). In all cases, the formation of the final reaction products is independent of the reagent ratio and the type of the phase-transfer catalysis system ($K_2CO_3$/DMSO, $K_2CO_3$/MeCN, or NaOH(aq.)/$CH_2Cl_2$), although equimolar reagent ratios, potassium carbonate as the base, and acetonitrile as the solvent are most convenient to use at a rather high reaction rate and in view of the ease of product isolation.

As expected, in the presence of two mutually *ortho* bromomethyl groups in the electrophilic component, the reaction resulted in annelation of two saturated *gem*-functionalized cyclopentane rings with the benzene ring (Scheme 2).

**Scheme 2**




$R^1 = R^2$ = Ph (**a**); $R^1$ = Ph, $R^2$ = OEt (**d**)

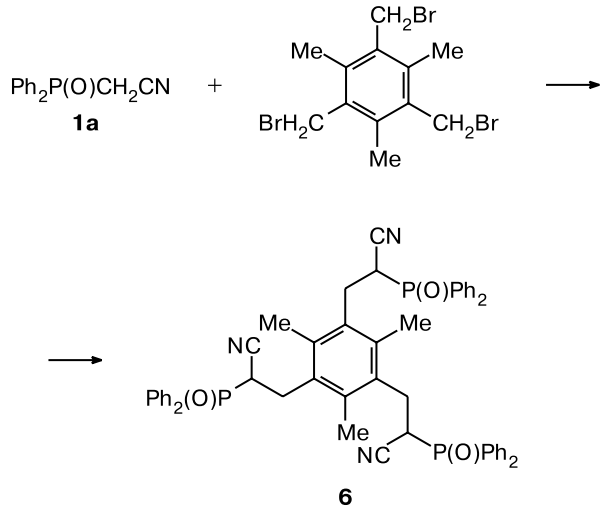
By contrast, the reaction of (thio)phosphorylacetonitriles with 1,2,3,4-tetrakis(bromomethylbenzene) proceeds nonselectively to yield a mixture of various monoalkylation and cycloalkylation products and oligomeric compounds (due to dialkylation). However, we failed to isolate individual compounds in this case.

As mentioned above, the reactions of diphenylphosphoryl- and diphenylthiophosphorylacetonitriles **1a,b** with hexakis(bromomethyl)benzene proceed as exhaustive cycloalkylation to form *cis*,*cis* and *trans*,*cis* isomers of 2,5,8-tris(diphenyl(thio)phosphoryl)-2,3,4,5,6,7,8,9-octahydro-1*H*-cyclopent[*e*]-as-indacene-2,5,8-tricarbonitriles (tris-phosphorylated triindanes).[12] This result is, apparently, attributable not only to the fact that the five-membered ring closure is thermodynamically more favorable but also to high symmetry of the final products.

It should be noted that the reactions of compounds containing three *meta*-arranged bromomethyl groups in the benzene ring (sterically separated by methyl groups), like the reactions of phosphorus-substituted CH-acids with bromomethylarenes and 1,4-bis(bromomethyl)benzene, occur as triple monoalkylation to give tris-phosphorylated benzene **6** (Scheme 3).

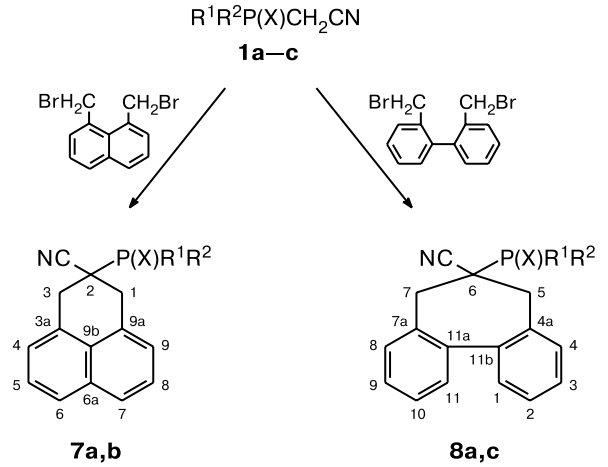
It is known that five-membered rings are thermodynamically most favorable and are generally easily formed. Six-membered rings are slightly less favorable. The syn-

**Scheme 3**




thesis of seven-membered rings is less selective. However, alkylation of (thio)phosphorylacetonitriles **1a—c** with 1,8′-bis(bromomethyl)naphthalene or 2,2′-bis(bromomethyl)-1,1′-biphenyl affords cycloalkylation products **7a,b** and **8a,c** in high yields (Scheme 4).

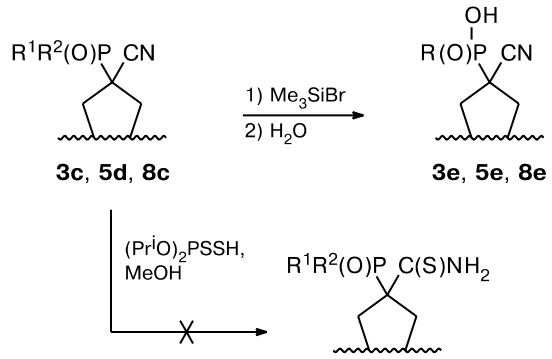
**Scheme 4**




$R^1 = R^2$ = Ph, X = O (**a**); $R^1 = R^2$ = Ph, X = S (**b**); $R^1 = R^2$ = OEt, X = O (**c**)

The investigation of the chemical properties of the resulting fused nitriles showed that the cyano group in these compounds is inactive. For example, this group is not transformed into the thioamide under the action of diisopropyldithiophosphoric acid, in contrast to (thio)phosphorylacetonitriles and products of their reactions with 1,4-bis(bromomethyl)benzenes.[14] For these compounds, alkoxy substituents at the phosphorus atom can be easily modified to prepare the corresponding phosphorus acids **3e**, **5e**, and **8e** (87—93% yields) containing various cyclic moieties (Scheme 5).

**Scheme 5**




R = OH (**3e**, **8e**), Ph (**5e**)

Acids **3e**, **5e**, and **8e** are high-melting crystalline compounds having low solubility both in organic solvents (including DMSO) and water.

The compositions and structures of the compounds were confirmed by elemental analysis and IR and NMR spectroscopy (Tables 1 and 2). In addition, we studied selected fused phosphorus-substituted derivatives containing rings of different sizes and characterized by the same substitution environment about the phosphorus atom (compounds **4a**, **7a**, and **8a**) by X-ray diffraction. We found that the "phosphorus-containing unit," *viz.*, the $Ph_2P(O)—C—(CN)$ fragment, in these compounds has virtually the same structure (Figs 1—3, Table 3). In all three compounds, the cyano group is antiperiplanar to the phosphoryl group. The O(1)—P(1)—C(1)—C(4) torsion angle ($\phi$) varies in the range of 171.6—176.5°.

To estimate whether the antiperiplanar conformation about the P(1)—C(1) bond observed in the crystals actually corresponds to the energy minimum, we performed quantum-chemical PBE/Tz2P calculations for compound **2a**. The calculations for two conformations, *viz.*, the synperiplanar (sp) conformation with $\phi$ = 74.9° and the antiperiplanar (ap) conformation with $\phi$ = 179.7°, showed that the ap conformation of both the isolated molecules and the molecules in the crystals corresponds to the energy minimum and is energetically more favorable by 4.67 kcal $mol^{-1}$. It should be noted that the sp conformation is characterized by the larger dipole moment (6.07 D) compared to that of the ap conformation (1.23 D). Taking into account this fact, in spite of a considerable difference in the energy of the conformers, it can be hypothesized that the sp conformer can exist along with the ap conformer in solutions of high polarity.

The five-membered C(2)C(1)C(3)C(6)C(5) ring in **4a** adopts an envelop conformation (the deviation of the C(1) atom is 0.40 Å). The six-membered

**Table 1.** Yields, physicochemical constants, elemental analysis data, and IR and $^{31}P$ NMR spectroscopic data for cycloalkylated (thio)phosphorylacetonitriles

| Compound | X | $R^1$, $R^2$ | Yield (%) | M.p./°C (solvent) | Found / Calculated (%) C | H | N | Molecular formula | IR, ν/cm$^{-1}$ CN | $CH_2$[a] | P=O | $\delta_P$ ($CDCl_3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **2a** | O | $Ph_2$ | 58 | 80 ($Et_2O$/hexane) | 76.81<br>76.51 | 5.87<br>5.84 | 4.05<br>4.06 | $C_{22}H_{18}NOP$ | 2227 | 1437 | 1202 | 29.30 |
| **2b** | S | $Ph_2$ | 47 | 113—114 ($CH_2Cl_2$/$Et_2O$) | 73.33<br>73.11 | 5.46<br>5.58 | 3.54<br>3.88 | $C_{22}H_{18}NSP$ | 2230 | 1440 | 658[b] | 55.13 |
| **3a** | O | $Ph_2$ | 58 | 180—181 ($CH_2Cl_2$/$Et_2O$/petroleum ether) | 79.17<br>79.38 | 5.14<br>5.12 | 3.56<br>3.56 | $C_{26}H_{20}NOP$ | 2230 | 1445 | 1205 | 28.78 |
| **3c** | O | $(OEt)_2$ | 68 | 114—115[c] | 65.62<br>65.65 | 6.06<br>6.12 | 4.26<br>4.25 | $C_{18}H_{20}NO_3P$ | 2231 | 1437 | 1257[d] | 21.40 |
| **3e** | O | $(OH)_2$ | 90 | 260—261 | 59.28<br>59.58 | 4.81<br>4.63 | 4.67<br>4.96 | $C_{18}H_{20}NO_3P$[e] | 2240 | 1433 | 1207[f] (br) | 16.99[f] |
| **4a** | O | $Ph_2$ | 73 | 204—205 ($CH_2Cl_2$/$Et_2O$) | 78.55<br>79.38 | 5.04<br>5.12 | 3.44<br>3.56 | $C_{26}H_{20}NOP$ | 2227 | 1435, 1439 | 1195 | 29.74 |
| **4b** | S | $Ph_2$ | 68 | 238—239 ($CH_2Cl_2$/EtOH) | 76.55<br>76.26 | 5.04<br>4.92 | 3.44<br>3.42 | $C_{26}H_{20}NSP$ | 2225 | 1438 | 652[b] | 55.81 |
| **5a** | O | $Ph_2$ | 50 | 270 (decomp.) ($CH_2Cl_2$/$Et_2O$) | 74.36<br>74.74 | 4.83<br>5.28 | 4.32<br>4.59 | $C_{38}H_{30}N_2O_2P_2$[e] | 2228 | 1438 | 1202 | 29.02 (*cis*)<br>29.08 (*trans*) |
| **5d** | O | OEt, Ph | 67 | 250—251 (EtOH/$Et_2O$) | 63.27<br>63.04 | 5.49<br>5.80 | 4.90<br>5.14 | $C_{30}H_{30}N_2O_4P_2 \cdot 1.5H_2O$ | 2235 | 1438, 1440 | 1230, 1232[d] | 36.15 |
| **5e** | O | OH, Ph | 87 | 335—336 | 63.27<br>63.04 | 5.49<br>5.80 | — | $C_{26}H_{22}N_2O_4P_2 \cdot 4H_2O$ | 2234 | 1438 | 1226, 1187, 1181 | 30.29[g] |
| **6** | O | $Ph_2$ | 65 | 213—214 ($CH_2Cl_2$/$Et_2O$) | 69.41<br>69.45 | 5.34<br>5.83 | 4.37<br>4.50 | $C_{54}H_{48}N_3O_3P_3 \cdot 3H_2O$ | 2236 | 1438 | 1210 | 28.18 (P(2))<br>28.26 (P(1)) |
| **7a** | O | $Ph_2$ | 66 | 295 ($CH_2Cl_2$/$Et_2O$) | 78.88<br>79.38 | 4.93<br>5.12 | 3.56<br>3.56 | $C_{26}H_{20}NOP$ | 2230[h] | 1445 | 1200 | 24.76 |
| **7b** | S | $Ph_2$ | 57 | 220—225 (decomp.) ($CH_2Cl_2$/$Et_2O$) | 76.35<br>76.26 | 4.72<br>4.92 | 3.45<br>3.42 | $C_{26}H_{20}NSP$ | 2230[h] | 1448 | 660[d] | 53.13 |
| **8a** | O | $Ph_2$ | 74 | 190—191 ($CH_2Cl_2$/$Et_2O$) | 80.41<br>80.18 | 5.43<br>5.28 | 3.38<br>3.81 | $C_{28}H_{22}NOP$ | 2225 | 1445 | 1203 | 28.43 |
| **8c** | O | $(OEt)_2$ | 78 | Oil[b] | 67.64<br>67.60 | 6.40<br>6.24 | 3.82<br>3.94 | $C_{20}H_{22}NO_3P$ | 2229 | 1440 | 1255 | 21.03 |
| **8e** | O | $(OH)_2$ | 93 | 253—254 | 62.79<br>62.34 | 5.21<br>4.90 | 4.32<br>4.54 | $C_{16}H_{14}NO_3P_2 \cdot 0.5H_2O$[e] | 2241 | 1444 | 1161 (br)[f] | 16.43[g] |

[a] Bending vibrations.
[b] Absorption of the P=S group.
[c] Purified by chromatography.
[d] ν(P—O—C) 1039, 1027 (**3c**); 1032 cm$^{-1}$ (**5d**).
[e] Found/calculated P (%): 10.56/10.97 (**3e**); 9.89/10.18 (**5a**); 9.67/10.00 (**8e**).
[f] ν(P—OH) 1015 (**3e**); 1024, 1004 cm$^{-1}$ (**8e**).
[g] In DMSO-$d_6$.
[h] A very weak band.

C(2)C(1)C(3)C(7)C(6)C(5) ring in **7a** assumes a half-chair conformation (the deviation of the C(1) atom is 0.65 Å). The seven-membered C(3)C(1)C(2)C(5)C(6)C(11)C(12) ring in **8a** is in a distorted boat conformation (the C(2),C(11), and C(12) atoms deviate from the mean plane by 0.58, 1.10, and 1.01 Å, respectively). The dihedral angle between the phenyl rings in the biphenyl fragment of **8a** is 50.1°, which is, in principle, characteristic of biphenyls, which contain a fused seven-membered aliphatic ring and have no organophosphorus substituents.[15] In all the compounds under study, the phosphorus-containing substituent and the CN group

**Table 2.** Parameters of $^1$H and $^{13}$C NMR spectra ($CDCl_3$) of compounds 


| Compound | $^1$H NMR (δ, *J*/Hz) | $^{13}$C NMR (δ, *J*/Hz) | | | | |
|---|---|---|---|---|---|---|
| | | PCCN ($^1J_{P,C}$) | $CH_2$ | CN ($^2J_{P,C}$) | $R^1$, $R^2$ | Arylene |
| **2a** | 3.28 ($H_B$), 3.91 ($H_A$) ABX (2 $H_{trans}$ + 2 $H_{cis}$, $^2J_{H,H}$ = 15.6, $^3J_{P,HB}$ = 2.4, $^3J_{P,HA}$ = 8.0); 7.15—7.21 (m, 4 H, $C_6H_4$); 7.55—7.60 (m, 4 H, *m*-Ph, PhP); 7.63—7.67 (m, 2 H, *p*-Ph, PhP); 8.07—8.12 (m, 4 H, *o*-Ph, PhP) | 42.53 (69.3) | 39.70 | 122.68 (1.9) | 128.74 (d, *m*-CH, PhP, $^3J_{P,C}$ = 12.1); 129.04 (d, $C_{ipso}$, PhP, $^1J_{P,C}$ = 101.2); 131.71 (d, *o*-CH, PhP, $^2J_{P,C}$ = 8.9); 132.78 (d, *p*-CH, PhP, $^4J_{P,C}$ = 2.7) | 124.29 (4,7-$C_6H_4$); 127.41 (5,6-$C_6H_4$); 138.12 (d, C(3a), C(7a), $C_6H_4$, $^3J_{P,C}$ = 7.1) |
| **2b** | 3.31 ($H_B$), 4.13 ($H_A$) ABX (2 $H_{trans}$ + 2 $H_{cis}$, $^2J_{H,H}$ = 16.0, $^3J_{P,HB}$ = 4.0, $^3J_{P,HA}$ = 16.0); 7.15—7.23 (m, 4 H, $C_6H_4$); 7.55—7.67 (m, 6 H, *m*-Ph, *p*-Ph, PhP); 8.08—8.18 (m, 4 H, *o*-Ph, PhP) | — | — | — | — | — |
| **3a** | 3.38 ($H_B$), 4.04 ($H_A$) ABX (2 $H_{trans}$ + 2 $H_{cis}$, $^2J_{H,H}$ = 15.6, $^3J_{P,HB} \leq 0.5$, $^3J_{P,HA}$ = 12.0); 7.42—7.51 (m, 2 H, C(6)H, C(7)H, $C_{10}H_6$); 7.57—7.69 (m, 2 H + 6 H, C(1)H, C(4)H, $C_{10}H_6$ + *m*-Ph, *p*-Ph, PhP); 7.72—7.78 (m, 2 H, C(5)H, C(8)H, $C_{10}H_6$); 8.13 (dd, 4 H, *o*-Ph, PhP, $^3J_{P,H}$ = 11.6, $^3J_{H,H}$ = 3.9) | 43.64 (69.8) | 39.14 ($^2J_{P,C}$ = 4.3) | 122.40 (0.9) | 128.80 (d, *m*-CH, PhP, $^3J_{P,C}$ = 12.2); 129.01 (d, $C_{ipso}$, PhP, $^1J_{P,C}$ = 101.8); 131.73 (d, *o*-CH, PhP, $^2J_{P,C}$ = 8.9); 132.86 (d, *p*-CH, PhP, $^4J_{P,C}$ = 2.5) | 122.94 (C(4), C(9)); 125.59 (C(5), C(8)); 127.74 (C(6), C(7)); 133.06 (C(4a), C(8a)); 136.81 (d, C(3a), C(9a), $^3J_{P,C}$ = 7.7) |
| **3c** | 1.38 (t, 6 H, Me, $^3J_{H,H}$ = 7.2); 3.63 ($H_B$), 3.81 ($H_A$) ABX (2 $H_{trans}$ + 2 $H_{cis}$, $^2J_{H,H}$ = 16.2, $^3J_{P,HB}$ = 7.2, $^3J_{P,HA}$ = 15.6); 4.24—4.32 (m, 4 H, $OCH_2$); 7.45—7.46 (m, 2 H, C(6)H, C(7)H, $C_{10}H_6$); 7.71 (s, 2 H, C(1)H, C(4)H, $C_{10}H_6$); 7.78—7.80 (m, 2 H, C(5)H, C(8)H, $C_{10}H_6$) | 40.77 (152.6) | 39.93 | 120.31 (5.3) | 16.17 (d, Me, $^3J_{P,H}$ = 5.2); 64.00 (d, $OCH_2$, $^2J_{P,C}$ = 6.9) | 122.81 (C(4), C(9)); 125.61 (C(5), C(8)); 127.44 (C(6), C(7)); 132.97 (C(4a), C(8a)); 136.76 (d, C(3a), C(9a), $^3J_{P,C}$ = 9.2) |
| **3e**[a] | 3.52 ($H_B$), 3.61 ($H_A$) ABX (2 $H_{trans}$ + 2 $H_{cis}$, $^2J_{H,H}$ = 16.0, $^3J_{P,HB}$ = 5.6, $^3J_{P,HA}$ = 16.4); 7.45—7.48 (m, 2 H, C(6)H, C(7)H, $C_{10}H_6$); 7.82 (s, 2 H, C(1)H, C(4)H, $C_{10}H_6$); 7.85—7.87 (m, 2 H, C(5)H, C(8)H, $C_{10}H_6$) | — | — | — | — | — |

(*to be continued*)

**Table 2** (*continued*)

| Compound | $^1$H NMR (δ, *J*/Hz) | $^{13}$C NMR (δ, *J*/Hz) | | | | |
|---|---|---|---|---|---|---|
| | | PCCN ($^1J_{P,C}$) | $CH_2$ | CN ($^2J_{P,C}$) | $R^1$, $R^2$ | Arylene |
| **4a** | 3.49 (d, 1 H, $CH_B$, $^2J_{H,H}$ = 16.0); 3.73 (d, 1 H, $CH_B$, $^2J_{H,H}$ = 16.0); 4.11, 4.19 (both dd, 1 $H_A$ each, $CH_2$, $^2J_{H,H}$ = 16.0, $^3J_{P,H}$ = 14.4); 7.30 (d, 1 H, $C_6H_2$, *J* = 8.4); 7.45—7.50 (m, 2 H, $C_6H_4$); 7.55—7.67 (m, 1 H($C_{Ar}$) + 6 H, *p*-Ph, *m*-Ph, PhP); 7.73 (d, 1 H, $C_6H_4$, *J* = 7.6); 7.84 (d, 1 H, $C_6H_4$, *J* = 7.6); 8.11—8.19 (m, 4 H, *o*-Ph, PhP) | 41.83 (68.6) | 38.78, 40.96 | 122.95 (1.9) | 128.41 (d, *o*-CH, PhP, $^3J_{P,C}$ = 8.0); 129.13 (d, $C_{ipso}$, PhP, $^1J_{P,C}$ = 101.2); 131.80, 131.84 (both d, *m*-CH, PhP, $^2J_{P,C}$ = 9.1); 132.82, 132.85 (both d, *p*-CH, Ph, $^4J_{P,C}$ = 2.6) | 122.05, 123.58, 125.48, 126.47 128.63, 128.73, 128.79, 128.85 (Ar); 133.90 (d, C(3a), $^3J_{P,C}$ = 6.5); 135.47 (d, C(9a), $^3J_{P,C}$ = 6.6) |
| **4b** | 3.49 (dd, 1 H, $CH_B$, $^2J_{H,H}$ = 16.2, $^3J_{P,H}$ = 3.6); 3.74 (dd, 1 H, $CH_B$, $^2J_{H,H}$ = 16.2, $^3J_{P,H}$ = 3.2); 4.26 (t, 1 H, $CH_A$, $^2J_{H,H}$ = $^3J_{P,H}$ = 16.2); 4.35 (t, 1 H, $CH_A$, $^2J_{H,H}$ = $^3J_{P,H}$ = 16.2); 7.30 (d, 1 H, $C_6H_2$, *J* = 8.8); 7.45—7.50 (m, 2 H, $C_6H_4$); 7.55—7.67 (m, 1 H + 6 H, *p*-Ph, *m*-Ph, PhP); 7.73 (d, 1 H, $C_6H_4$, *J* = 8.8); 7.85 (d, 1 H, $C_6H_4$, *J* = 6.8); 8.14—8.19 (m, 4 H, *o*-Ph, PhP) | 43.60 (51.3) | 40.49 (br.d, $^2J_{P,C}$ = 13.8); 42.67 (br.d, $^2J_{P,C}$ = 13.8) | 123.10 | 128.56, 128.85, 128.91, 128.92 (all d, 4 *o*-CH, PhP, $^3J_{P,C}$ = 8.0); 126.00 (d, $C_{ipso}$, PhP, $^1J_{P,C}$ = 102.3); 126.20 (d, $C_{ipso}$, PhP, $^1J_{P,C}$ = 101.7); 132.36, 132.39 (both d, *m*-CH, PhP, $^2J_{P,C}$ = 10.5); 132.48, 132.87 (*p*-CH, Ph) | 121.98, 122.21, 123.64, 123,80, 128.43, 128.92, 129.58, 132.87 (Ar); 133.90 (d, C(3a), $^3J_{P,C}$ = 7.1); 135.46 (d, C(9a), $^3J_{P,C}$ = 7.0) |
| **5a** | 3.16 (m, 4 H, *trans*-$CH_2$); 3.81 (m, 4 H, *cis*-$CH_2$); 6.90 (s, 2 H, $C_6H_2$); 7.53—7.58 (m, 8 H, *m*-Ph, PhP); 7.61—7.66 (m, 4 H, *p*-Ph, PhP); 8.06 (dd, 8 H, *o*-Ph, PhP, $^3J_{H,H}$ = 8.4, $^3J_{P,H}$ = 10.4) | 43.03 (69.3) | 39.35 | 122.54 | 128.85 (d, *m*-CH, PhP, $^3J_{P,C}$ = 12.2); 129.00 (d, $C_{ipso}$, PhP, $^1J_{P,C}$ = 101.8); $^3J_{P,C}$ = 6.8); 131.81 (d, *o*-CH, PhP, $^2J_{P,C}$ = 8.9); 132.89 (*p*-CH, PhP) | 120.55 (C(4), C(8)); 138.24 (d, C(3a), C(8a), C(4a), C(7a), $^3J_{P,C}$ = 6.8) |
| **5d** | 1.39 (dt, 6 H, Me, $^3J_{H,H}$ = 6.1); 2.95—3.06, 3.78—3.86 (both m, 2 H each, $CH_2CP$); 3.26—3.58, 4.07—3.25 (both m, 4 H each, $CH_2O$); 6.87 (s, 2 H, Ar); 7.56 (s, 4 H, *m*-Ph, PhP); 7.67 (s, 4 H, *p*-Ph, PhP); 7.95, 7.97 (both d, 4 H, *o*-Ph, PhP) | 43.08 (101.6) | 38.78, 39.41 | 121.33 | 16.31 (d, Me, $^3J_{P,C}$ = 5.1); 62.07 (d, $CH_2O$, $^2J_{P,C}$ = 6.4); 126.65 (d, $C_{ipso}$, PhP, $^1J_{P,C}$ = 130.5); 128.81 (d, *m*-CH, PhP, $^3J_{P,C}$ = 13.1); 132.93 (d, *o*-CH, PhP, $^2J_{P,C}$ = 9.4); 133.54 (*p*-CH, PhP) | 127.30, 126.00 (C(4), C(8)); 137.92 (d, C(3a), C(8a), $^3J_{P,C}$ = 8.5); 138.48 (d, C(4a), C(7a), $^3J_{P,C}$ = 7.2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| **5e**[a] | 3.49 ($H_B$), 3.52 ($H_A$), ABX (4 $H_{trans}$ + 4 $H_{cis}$, $^2J_{H,H}$ = 16.4, $^3J_{P,HB} \le 0.5$, $^3J_{P,HA}$ = 16.4); 7.58—7.60 (m, 4 H, *m*-Ph, PhP); 7.65—7.69 (m, 2 H, *p*-Ph, PhP); 7.83—7.86 (m, 4 H, *o*-Ph, PhP) | — | — | — | — | — |
| **7a** | 3.22 ($H_B$), 3.89 ($H_A$) ABX (2 $H_{trans}$ + 2 $H_{cis}$, $^2J_{H,H}$ = 15.6, $^3J_{P,HB}$ = 4.4, $^3J_{P,HA}$ = 6.0); 7.21 (d, 2 H, C(2)H, C(7)H, Ar, $^3J_{H,H}$ = 6.8); 7.39 (t, 2 H, C(3)H, C(6)H, Ar, $^3J_{H,H}$ = 6.8); 7.60—7.68 (m, 6 H, *p*-Ph, *m*-Ph, PhP); 7.74 (d, 2 H, C(4)H, C(5)H, Ar, $^3J_{H,H}$ = 6.8); 8.23—8.27 (m, 4 H, *o*-PhP) | 37.72 (67.2) | 33.75 | 120.43 | 128.21 (d, $C_{ipso}$, PhP, $^1J_{C,P}$ = 100.2); 128.94 (d, *m*-CH, PhP, $^3J_{P,C}$ = 11.9); 132.12 (d, *o*-CH, PhP, $^2J_{P,C}$ = 8.6); 132.92 (*p*-CH, PhP, $^4J_{P,C}$ = 2.6) | 125.44 (C(4), C(5)); 125.69 (C(8), C(9)); 127.31 (C(6), C(7)); 128.10 (C(6a)); 129.03 (d, C(3a), C(9a), $^3J_{P,C}$ = 7.6); 133.24 (C(9b)) |
| **7b** | 3.17 ($H_B$), 4.08 ($H_A$) ABX (2 $H_{trans}$ + 2 $H_{cis}$, $^2J_{H,H}$ = 15.6, $^3J_{P,HB}$ = 4.0, $^3J_{P,HA}$ = 7.6); 7.21 (d, 2 H, C(2)H, C(7)H, Ar, $^3J_{H,H}$ = 6.8); 7.39 (t, 2 H, C(3)H, C(6)H, Ar, $^3J_{H,H}$ = 8.0); 7.58—7.68 (m, 6 H, *p*-Ph, *m*-Ph, PhP); 7.73 (d, 2 H, C(4)H, C(5)H, Ar, $^3J_{H,H}$ = 8.0); 8.32—8.38 (m, 4 H, *o*-PhP); | 39.23 (50.7) | 34.74 | 120.67 | 127.98 (d, $C_{ipso}$, PhP, $^1J_{C,P}$ = 80.6); 128.77 (d, *m*-CH, PhP, $^3J_{P,C}$ = 12.13); 132.61 (*p*-CH, PhP, $^4J_{P,C}$ = 2.8); 132.85 (d, *o*-CH, PhP, $^2J_{P,C}$ = 9.6) | 125.41 (C(4), C(5)); 125.72 (C(8), C(9)); 127.23 (C(6), C(7)); 127.96 (C(6a)); 129.15 (d, C(3a), C(9a), $^3J_{P,C}$ = 11.2); 133.16 (C(9b)) |
| **8a** | 2.61, 3.31 (both br.m, 2 H each, $CH_2$); 7.22—7.27 (d, 2 H, Ar, $^3J_{H,H}$ = 8.8); 7.31—7.35 (two t, 2 H, Ar, $^3J_{H,H}$ = 8.8); 7.37—7.43 (m, 4 H, Ar); 7.56—7.64 (m, 6 H, *p*-Ph, *m*-Ph, PhP); 8.15—8.27 (br.s, 4 H, *o*-Ph, PhP) | 47.78 (63.5) | 35.57 | 121.44 | 128.79 (d, *m*-CH, PhP, $^3J_{P,C}$ = 11.9); 130.15 (d, $C_{ipso}$, PhP, $^1J_{P,C}$ = 80.1); 131.99 (d, *o*-CH, PhP, $^2J_{P,C}$ = 8.3); 132.62 (*p*-CH, PhP) | 127.74 (C(1), C(11)); 128.13 (C(2), C(10)); 128.21 (C(3), C(4), C(8), C(9)); 132.76 (d, C(4a), C(7a), $^3J_{P,C}$ = 6.6); 139.98 (s, C(11a), C(11b)) |
| **8c** | 1.31 (t, 6 H, Me, $^3J_{H,H}$ = 6.8); 2.95 (br.s, 2 H, $CH_2$, $^3J_{P,H}$ = 14.0); 3.10 (br.s, 2 H, $CH_2$); 4.24 (dq, 4 H, $OCH_2$, $^3J_{P,H}$ = 14.4, $^3J_{H,H}$ = 6.8); 7.35—7.41 m (8 H, Ar) | 46.60 (143.2) | 35.89 | 119.20 (6.2) | 16.12 (d, Me, $^3J_{P,C}$ = 5.5); 63.89 (d, $OCH_2$, $^2J_{P,C}$ = 6.7) | 127.60 (C(1), C(11)); 128.19 (C(2), C(3), C(4), C(8), C(9), C(10)); 132.68 (d, C(4a), C(7a), $^3J_{P,C}$ = 6.6); 140.09 (C(11a), C(11b)) |
| **8e**[a] | 2.75—2.79 m + 3.45 br.s (2 H each, $CH_2$); 7.36, 7.44 (both s, 8 H, Ar) | — | — | — | — | — |

[a] In DMSO-$d_6$.

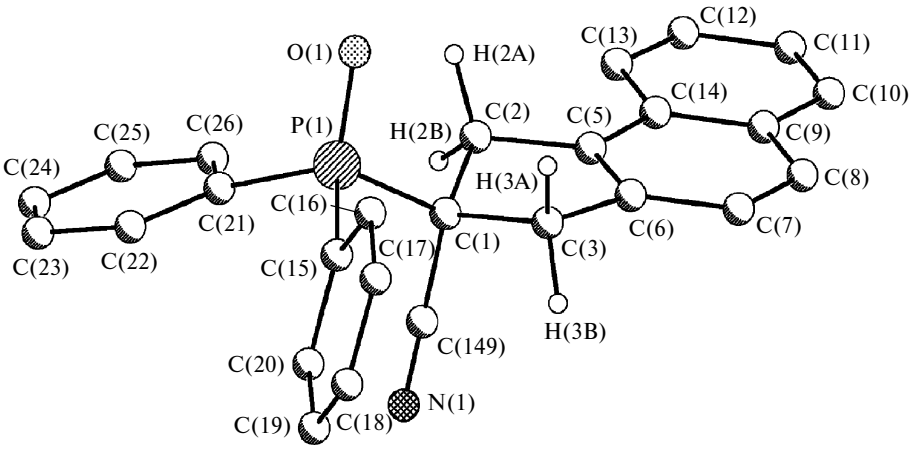



**Fig. 1.** Overall view of molecule **4a**.

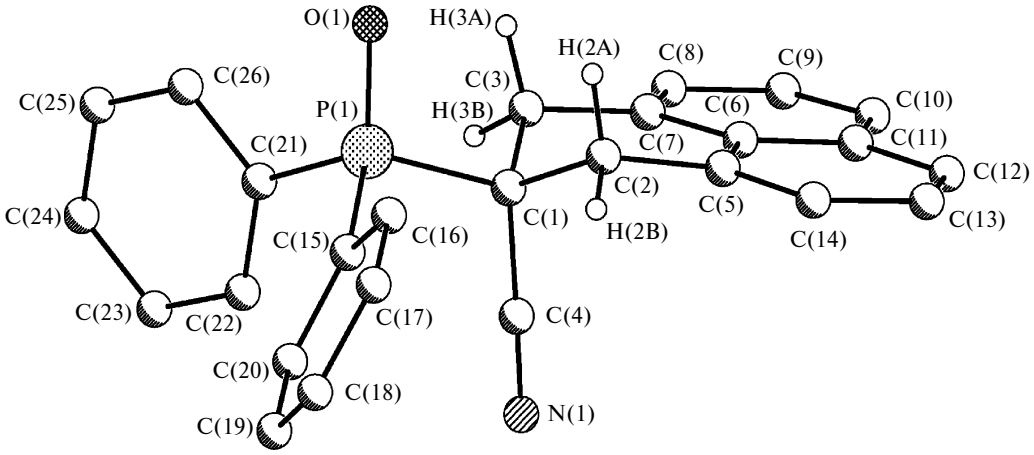



**Fig. 2.** Overall view of molecule **7a**.

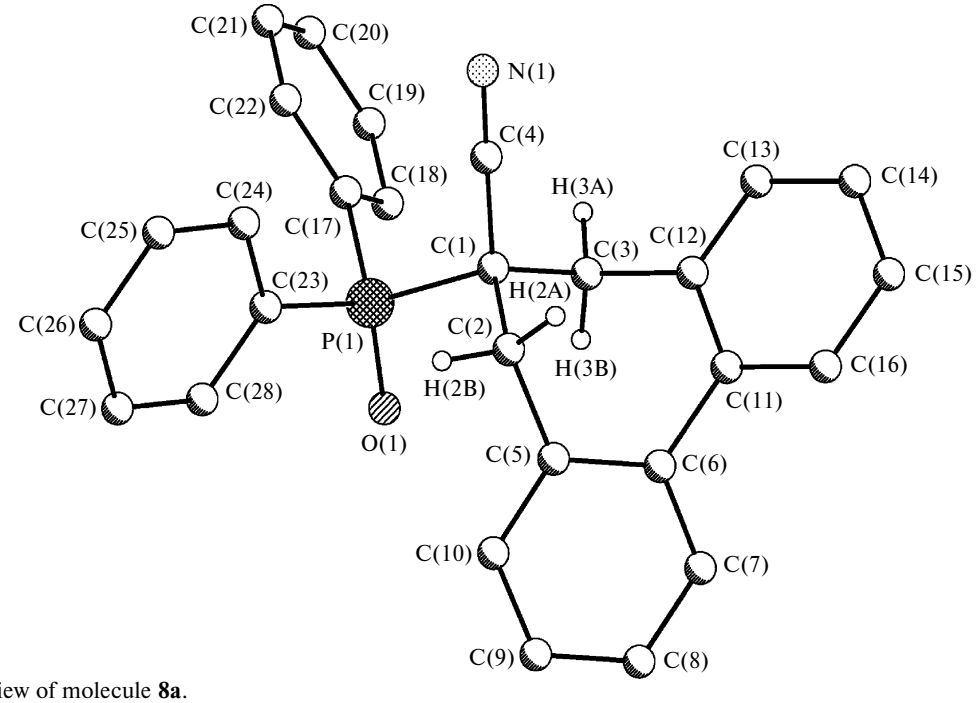



**Fig. 3.** Overall view of molecule **8a**.

**Table 3.** Selected bond lengths (*d*), bond angles (ω), and the torsion angle (ϕ) in compounds **4a**, **7a**, and **8a**

| Parameter | **4a** | **7a** | **8a** |
|---|---|---|---|
| Bond | | *d*/Å | |
| P(1)—O(1) | 1.476(2) | 1.476(2) | 1.487(2) |
| P(1)—C(1) | 1.850(2) | 1.851(2) | 1.879(2) |
| P(1)—Ph | 1.800(2)—1.804(2) | 1.793(2)—1.798(3) | 1.804(2)—1.813(2) |
| C(1)—C(4) | 1.479(3) | 1.478(3) | 1.470(2) |
| C(4)—N(1) | 1.135(3) | 1.130(3) | 1.150(2) |
| Angle | | ω/deg | |
| O(1)—P(1)—C(1) | 109.6(1) | 107.9(1) | 109.46(7) |
| O(1)—P(1)—Ph | 112.7(1)—114.4(1) | 107.9(1)—113.1(1) | 111.82(8)—112.78(8) |
| C(1)—P(1)—Ph | 104.3(1)—107.2(1) | 107.0(1)—107.2(1) | 106.63(8)—106.85(8) |
| | | ϕ/deg | |
| N(1)—C(4)—P(1)—O(1) | 171.6 | 176.5 | 171.7 |

are in the equatorial and axial positions, respectively, which is, apparently, associated with the larger steric volume of the former substituent.

Analysis of the crystal packing demonstrated that weak C—H...O=P and C—H...NC interactions are the main crystal-forming contacts. In spite of the presence of the aromatic system, stacking interactions are absent in all the crystals under study.

The IR spectra of the compounds show characteristic absorption bands of the CN group at 2225—2230 $cm^{-1}$. In most cases, this band is in the moderate-intensity range, but in the spectra of compounds **7a,b** containing the annelated six-membered ring, this band is very weak. This type of compounds is characterized by bending vibrations of the $CH_2$ fragment at 1437—1448 $cm^{-1}$ and P=O absorption, which shifts to lower frequencies with increasing number of P—C bonds in the environment about the phosphorus atom (1200—1205 $cm^{-1}$ for phosphine oxides **2a—8a**; 1230 and 1232 $cm^{-1}$ for phosphinate **5d**; 1250—1255 $cm^{-1}$ for phosphonates **3c** and **8c**). The spectra of the corresponding acids show a broad absorption band of the hydroxy groups at 3000 $cm^{-1}$ and several absorption maxima of the P=O groups (free and protonated).

The chemical shifts in the $^{31}P$ NMR spectra of compounds **2—7** are characteristic of this type of environment about the phosphorus atom. The presence of the fused ring in the α position with respect to the phosphorus atom results in a downfield shift of the signal compared to the signal of the starting CH-acids **1**. Earlier, we have observed a similar regularity, *i.e.*, a gradual downfield shift in the $^{31}P$ NMR spectra caused by the introduction of the α substituent into phosphorus-substituted CH-acids, in studies of alkylation and cycloalkylation of nitriles and esters of (thio)phosphorylacetic acids with α,ω-dihaloalkanes.[3,14] The investigation of 2,6-bis(diphenylphosphoryl)-1,2,3,5,6,7-hexahydro-*s*-indacene-2,6-dicarbonitrile (**5a**) by $^{31}P$ NMR spectroscopy demonstrated that this compound exists as *cis* and *trans* stereoisomers characterized by singlets with Δδ ~0.06. Although we failed to separate these stereoisomers by chromatography or fractional crystallization, general considerations suggest that the less sterically hindered *trans* isomer is the major one (*cis* : *trans* ≈ 2 : 8). Evidently, analog **5d** is also formed as a mixture of stereoisomers. However, the $^{31}P—\{^1H\}$ NMR spectrum of the product isolated from the reaction mixture shows only one signal.

The $^1H$ NMR spectra are in complete agreement with the above-described structures of the *gem*-disubstituted fused rings. The presence of the rigid cyclic moiety in the molecules results in the nonequivalence of the methylene protons in the cycloalkyl ring. It is known that the three-bond coupling constant (in our case, $^3J_{PH}$) has the maximum value for the dihedral angle of 180°, has the next maximum for the *cis* orientation (the dihedral angle of 0°), is close to zero for the dihedral angle of 90°, and increases for the *gauche* configuration (the dihedral angle varies from 60 to 120°). X-ray diffraction study of **4a**, **7a**, and **8a** and quantum-chemical calculations for **2a** (see above) allowed us to precisely estimate these angles and to assign the signal to the corresponding protons in the $^1H$ NMR spectra (Table 4).

In the $^1H$ NMR spectra of compounds **2a,b**, the methylene protons of the five-membered ring appear as an ABX system (two doublets of doublets). Since the constant $^3J_{PH}$ for the high-field signal (δ 3.28 for **2a** and δ 3.31 for **2b**) is substantially smaller, we assigned this signal to the protons located in the *trans* position with respect to the phosphoryl fragment relative to the plane of the fused ring (the corresponding torsion angle is close to 90°). Taking into account that the introduction of an additional benzene ring should not influence the conformation of the *gem*-disubstituted ring (2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene-2-carbonitriles **3a,c**), the same regularity should be retained. Actually, the signals of the $CH_2$ groups in **2a** and **3a** bearing the same phosphorus-

**Table 4.** Correlations between the spin-spin coupling constants $^3J_{P,H}$ and the torsion angles in compounds **2a**, **4a**, **7a**, and **8a**

| Compound | Angle/deg P(1)C(1)C(2)H(2)/ P(1)C(1)C(3)H(3) | Proton | $\delta_H$ | $^3J_{P,H}$ |
|---|---|---|---|---|
| **2a**[a] | 94.2/94.1 | *trans*-$H_B(2)/H_B(3)$ | 3.28 | 2.4 |
| | 25.5/25.5 | *cis*-$H_A(2)/H_A(3)$ | 3.91 | 8.0 |
| **4a** | 94.1/95.6 | *trans*-$H_B(2)/H_B(3)$ | 3.49/3.73 | ≤0.5 |
| | 25.6/27.6 | *cis*-$H_A(2)/H_A(3)$ | 4.11/4.19 | 14.4 |
| **7a** | 65.5/70.7 | *trans*-$H_B(2)/H_B(3)$ | 3.22 | 4.4 |
| | 51.9/46.6 | *cis*-$H_A(2)/H_A(3)$ | 3.89 | 6.0 |
| **8a** | 159.1/72.0 | $H_B(2)/H_B(3)$ | 2.61 (br) | [b] |
| | 42.3/45.6 | $H_A(2)/H_A(3)$ | 3.31 (br) | [b] |

[a] For compound **2a**, the parameters are given for the ap conformer (calculated by the PBE/TZ2p method).
[b] The spin-spin coupling constant was not determined.

containing fragment have similar positions. The existence of $^3J_{PH} \leq 0.5$ Hz for the high-field signal in the spectrum of **3a** indicates that the torsion angle for the transoid protons in **3a** is close to 90°. For its analog **3c**, the signals for the A and B protons are closer spaced, the signal for the cisoid proton being shifted downfield, and the signal for $H_{trans}$ being shifted upfield. The signals for the $H_A$ and $H_B$ protons of the methylene groups in the corresponding phosphinic acid **3e** are located at an even shorter distance (δ 3.52 for $H_A$ and δ 3.61 for $H_B$).

A more complex situation is observed for unsymmetrical 2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-2-carbonitriles **4a,b**. The spectra of these compounds show individual signals for all four methylene protons. For two high-field signals in the spectrum of **4a**, $^3J_{PH} \leq 0.5$ Hz (the corresponding dihedral angles are 94.1 and 95.6°, respectively; the *trans*-arrangement, H(2B) and H(3B) in Fig. 1). In the spectrum of compound **4b**, the spin-spin coupling with the *trans* proton is slightly larger, which is indicative of a larger deviation of this angle from 90° compared to that in its oxygen analog.

In the spectra of symmetrical indacenes **5a,d**, the multiplicity of the signals of the analogous groups of protons is complicated due to overlap of the signals for the $CH_2$ groups in two different rings, as well as in the isomeric products.

An analogous correlation between the dihedral angles, the coupling constants $^3J_{PH}$, and, correspondingly, the position of the signals for the *cis* and *trans* protons in the $^1$H NMR spectra is retained for 2,3-dihydro-1*H*-phenalene-2-carbonitriles **7a,b** containing the six-membered cycloalkyl fragment. However, the dihedral angles for the *cis* protons are rather close to those for the *trans* protons, which is reflected in the small difference in the three-bond coupling constants.

Therefore, in the five- and six-membered rings containing an exocyclic phosphorus substituent, the signal for the α-proton in the *cis* position with respect to the phosphorus atom is shifted downfield compared to the signal for the proton in the *trans* position.

In conformationally flexible 6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene-6-carbonitriles **8a,c**, the arrangement of the methylene protons in the annelated seven-membered ring is rather difficult to identify as either *cis* or *trans* (see Table 4, the P(1)—C(1)—C(2)—H(2) and P(1)—C(1)—C(3)—H(3) dihedral angles). These signals in the $^1$H NMR spectra appear as a broadened unresolved signal.

The $^{13}$C NMR spectra are also consistent with the described structures. The signal for the carbon atom bound to the phosphorus atom appears as a characteristic doublet at δ 37.8—47.8. A comparison with the starting CH-acids and their monoalkylation products, *viz.*, 1,4-bis(bromomethyl)arenes,[12] revealed a downfield shift of this signal, the shift being most pronounced for the compounds with the seven-membered ring. The shift for the compounds with the cyclopentane ring is less pronounced, and the smallest shifts are observed for 2-(thio)phosphoryl-2,3-dihydro-1*H*-phenalene-2-carbonitriles **7a,b**. The signals for the cyclic methylene carbon atoms generally appear as a singlet, except for unsymmetrical compounds **4a,b**.

Therefore, regardless of the ratio of the starting reagents, the type of the phase-transfer catalysis system, and the size of the resulting ring, the reactions of phosphoryl- and thiophosphorylacetonitriles with poly(bromomethyl)arenes containing closely-spaced bromomethyl groups occur as cycloalkylation. The exception is the nonregioselective reaction with 1,2,3,4-tetrakis(bromomethylbenzene).

## Experimental

The NMR spectra were recorded on a Bruker AMX-400 instrument in $CDCl_3$ using the signal of the residual 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 in the JMODECHO mode; the signals for the carbon atoms bearing odd and even numbers of protons have opposite polarities. The IR spectra were recorded on a Magna-IR 750 (Nicolet) Fourier-transform IR spectrometer (spectral resolution was 2 $cm^{-1}$; 128 scans) in KBr pellets.

The starting phosphorylacetonitriles **1a,c,d** were prepared by the Arbuzov rearrangement of the corresponding esters of trivalent phosphorus acids under the action of chloroacetonitrile according to a known procedure.[16] Thiophosphorylacetonitrile **1b** was synthesized by the reaction of the corresponding phosphoryl derivative with Lawesson's reagent.[17] Bromomethylarenes, *viz.*, 1,2-bis(bromomethyl)benzene,[18] 1,2-bis(bromomethyl)naphthalene,[19] 2,3-bis(bromomethyl)naphthalene,[20] 1,8-bis(bromomethyl)naphthalene,[21] 1,2,3,4- and 1,2,4,5-tetrakis(bromomethyl)benzenes,[22] 2,2′-bis(bromomethyl)-1,1′-biphenyl,[23] and 1,3,5-tris(bromomethyl)-2,4,6-trimethylben-

**Table 5.** Principal crystallographic characteristics and parameters of refinement of **4a**, **7a**, and **8a**

| Parameter | **4a** | **7a** | **8a** |
|---|---|---|---|
| Molecular formula | $C_{26}H_{20}NOP$ | $C_{26}H_{20}NOP$ | $C_{29}H_{22}NOP \cdot OCMe_2$ |
| Molecular weight | 393.40 | 393.40 | 477.51 |
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $P2_1/c$ | $P\bar{1}$ |
| $Z(Z')$ | 4(1) | 4(1) | 2(1) |
| $a$/Å | 8.057(1) | 12.681(2) | 9.382(2) |
| $b$/Å | 25.248(4) | 8.5286(15) | 10.655(2) |
| $c$/Å | 10.013(1) | 18.728(3) | 13.297(2) |
| α/deg | | | 68.239(3) |
| β/deg | 100.386(3) | 103.470(4) | 87.674(3) |
| γ/deg | | | 88.299(3) |
| $V$/Å$^3$ | 4781(3) | 1969.8(6) | 1233.4(4) |
| $d_{calc}$/g cm$^{-3}$ | 1.304 | 1.327 | 1.286 |
| μ/cm$^{-1}$ | 1.54 | 1.57 | 1.41 |
| $F(000)$ | 824 | 824 | 504 |
| $2\theta_{max}$/deg | 54 | 54 | 58 |
| Number of measured reflections | 16233 | 18257 | 12125 |
| ($R_{int}$) | (0.0505) | (0.0400) | (0.0373) |
| Number of independent reflections | 4345 | 4283 | 6355 |
| Number of observed reflections | 2121 | 2347 | 4631 |
| Number of parameters in refinement | 262 | 262 | 337 |
| $R_1$ | 0.0501 | 0.0553 | 0.0570 |
| $wR_2$ | 0.1118 | 0.1094 | 0.1313 |
| GOOF | 0.0975 | 0.997 | 1.047 |
| Residual electron density (min/max)/e Å$^{-3}$ | −0.175/0.269 | −0.243/0.186 | −0.348/0.540 |

zene,[24] were prepared according to known procedures by bromination of the corresponding methylarenes.

The physicochemical constants of the starting reagents are identical with the data published in the literature.

**Cycloalkylation of phosphoryl- and thiophosphorylacetonitriles with *o*-bis(bromomethyl)arenes and related compounds (general procedure).** A mixture of the corresponding CH-acid **1** (4.15 mmol), 1 equiv. of the corresponding bis(bromomethyl)arene (4.15 mmol), and a fourfold excess of potassium carbonate (2.3 g, 12.6 mmol) in acetonitrile (~30 mL) was stirred for 15—20 h. The reaction was monitored by $^{31}$P NMR spectroscopy (since some products are poorly soluble in MeCN, the monitoring was performed with the addition of $CH_2Cl_2$ (0.5 volume) to an aliquot of the suspension). After completion of the stirring, water (20 mL) was added, and the reaction mixture was extracted with dichloromethane. The combined organic extracts were additionally washed with water (10 mL), dried over $Na_2SO_4$, filtered, concentrated to dryness, and recrystallized or purified by chromatography. The yields, physicochemical constants, elemental analysis data, and spectroscopic parameters for the functionalized fused products are given in Tables 1 and 2.

The following cycloalkylation products were synthesized: 2-diphenylphosphoryl-2-indanecarbonitrile (**2a**), 2-diphenylthiophosphoryl-2-indanecarbonitrile (**2b**), 2-diphenylphosphoryl-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene-2-carbonitrile (**3a**), 2-diethoxyphosphoryl-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene-2-carbonitrile (**3c**), 2-diphenylphosphoryl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-2-carbonitrile (**4a**), 2-diphenylthiophosphoryl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-2-carbonitrile (**4b**), 2,6-bis(diphenylphosphoryl)-1,2,3,5,6,7-hexahydro-*s*-indacene-2,6-dicarbonitrile (**5a**), 2,6-bis(phenylethoxyphosphoryl)-1,2,3,5,6,7-hexahydro-*s*-indacene-2,6-dicarbonitrile (**5d**), 2-diphenylphosphoryl-2,3-dihydro-1*H*-phenalene-2-carbonitrile (**7a**), 2-diphenylthiophosphoryl-2,3-dihydro-1*H*-phenalene-2-carbonitrile (**7b**), 6-diphenylphosphoryl-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene-6-carbonitrile (**8a**), and 6-diethoxyphosphoryl-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene-6-carbonitrile (**8c**).

**1,3,5-Tris[2-cyano-2-(diphenylphosphoryl)ethyl]-2,4,6-trimethylbenzene (6)** was prepared in 65% yield according to a standard procedure from compound **1a** (723 mg, 6 mmol), 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (393 mg, 1 mmol), and potassium carbonate (1.65 g, 12 mmol). The reaction time was 12 h. $^1$H NMR ($CDCl_3$), δ: 2.08 + 2.09 + 2.10 (all s, 4 H + 2 H + 3 H*, a total of 9 H, Me); 3.13—3.24 (m, 6 H, $CH_2$); 3.04—3.49 (m, 3 H, CH); 7.45—7.64 (m, 18 H, Ph); 7.79—7.86 and 7.93—8.03 (both m, 6 H each, Ph).

**2-(Dihydroxyphosphoryl)-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene-2-carbonitrile (3e).** A solution of 2-(diethoxyphosphoryl)-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene-

* The signals correspond to the methyl groups in different stereoisomers of the compound, which differ in the configuration of the chiral carbon atoms.

2-carbonitrile (**3c**) (0.8 g, 2.43 mmol) and $Me_3SiBr$ (2.4 g, 15.7 mmol) in anhydrous chloroform (6 mL) was kept at room temperature for 36 h. Then the solution was slowly poured into 70% aqueous MeOH (13 mL), the reaction mixture was stirred for 30 min, and all volatile components were removed *in vacuo*. The residue was recrystallized from water containing 10% EtOH. Compound **3e** was obtained in a yield of 0.6 g (90%) as white crystals, m.p. 260 °C.

Phosphinic acid **5e** and phosphonic acid **8e** were prepared analogously. The physicochemical constants, elemental analysis data, and spectroscopic characteristics are given in Tables 1 and 2.

**X-ray diffraction study of compounds 4a, 7a, and 8a.** X-ray diffraction data sets were collected on a three-circle SMART CCD diffractometer (Mo-Kα, graphite monochromator, ω-scanning technique) at 120 K. Principal crystallographic parameters and characteristics of refinement are given in Table 5. Semiempirical absorption corrections were applied using equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares method against $F^2$ with anisotropic displacement parameters for nonhydrogen atoms. Analysis of difference electron density syntheses demonstrated that the carbonyl group of the acetone solvate molecule in the structure of **8a** is disordered over two positions with equal occupancies. The coordinates of the hydrogen atoms were calculated geometrically and refined using a riding model. All calculations were carried out using the SHELXTL PLUS 5.0 program package.[25]

Quantum-chemical calculations (PBE/TZ2P) for **2a** were carried out with the use of the RIRODA program.[26]

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