

2,5,8-Tris(diphenylphosphoryl)- and 2,5,8-tris(diphenylthiophosphoryl)-2,3,4,5,6,7,8,9-octahydro-1H-cyclopent[e]-*asym*-indacene-2,5,8-tricarbonitriles as a novel type of polycondensed systems

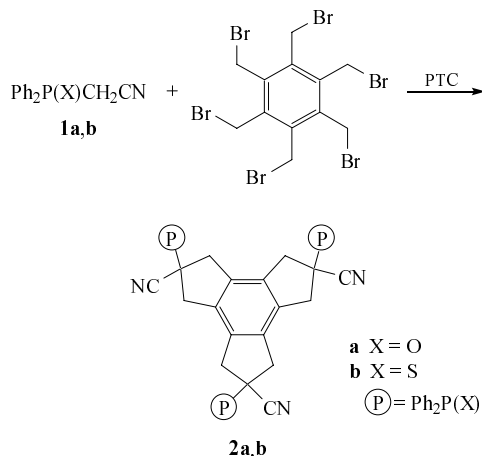
Irina L. Odinets,* Oleg I. Artyushin, Georgy V. Bodrin, Pavel V. Petrovskii and Tatyana A. Mastryukova

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation.
Fax: +7 095 135 5085; e-mail: odinets@ineos.ac.ru

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The interaction of phosphorylacetonitriles and thiophosphorylacetonitriles with hexakis(bromomethyl)benzene proceeds under phase-transfer catalysis conditions as exhausting cycloalkylation to form 2,5,8-tris(diphenylphosphoryl)- and tris(diphenylthiophosphoryl)-2,3,4,5,6,7,8,9-octahydro-1H-cyclopent[e]-*asym*-indacene-2,5,8-tricarbonitriles (tris-phosphorylated trindans).

The cycloalkylation of CH acids by linear α,ω -dihaloalkanes, which proceeds in the presence of bases, is known in organic chemistry as a main approach to 1,1-bifunctional substituted cyclic systems with three-membered or larger rings.¹ The reaction was performed under phase-transfer catalysis conditions (PTC).² A similar approach was also used to produce gem-disubstituted functionalised phosphorylated cycloalkanes^{3–11} using organometallic compounds as bases^{3–6} and phase-transfer⁷ or PTC^{8–11} conditions. In particular, we determined^{8,9} that corresponding gem-disubstituted cyclopropanes, butanes and pentanes can be easily produced in high yields from phosphoryl and thiophosphorylacetic acid nitriles and esters using the heterophase system K_2CO_3 /DMSO at 20 °C. Marr *et al.*⁴ reported that other heterophase systems [NaH/THF–DMSO (80:20, v/v) at 20 °C and K_2CO_3 /MeCN at 80 °C] give similar products. It was also found⁵ that thiophosphorylacetonitriles react (in accordance with the cycloalkylation mechanism) with linear α,ω -chlorobromoalkanes, in particular, with corresponding 1,2- and 1,4-derivatives (aq. NaOH/ CH_2Cl_2 ; s. KOH/MeCN). In order to obtain polyfunctional complexons and extracting agents of a novel type, precursors of phosphine ligands with fixed stereochemistry and molecules being the cores of the subsequent dendrimer formation, we studied the cycloalkylation of (thio)phosphorylacetonitriles **1** by hexakis(bromomethyl)benzene.



Although in the above process the formation of various products (e.g., C-mono, C,C-dialkylation and polymerization) would also be expected, the thermodynamic stability of five-membered rings and the high symmetry of products result in the reaction proceeding at a stoichiometric ratio between reactants according to the exhausting cycloalkylation mechanism to give corresponding trindans **2** in high yields.

The reaction was carried out at room temperature under PTC conditions in the system K_2CO_3 (or Cs_2CO_3)/MeCN–DMSO (95:5, v/v). When potassium carbonate was used as a base, the interaction was complete in 15–18 h, and the presence of caesium carbonate substantially accelerated the reaction. Note that

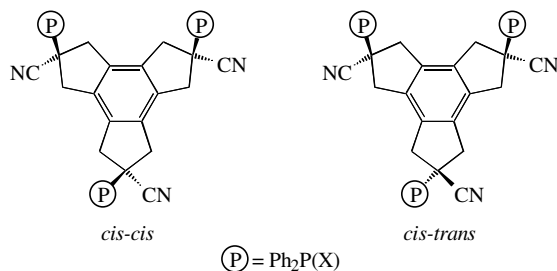
the rate of cycloalkylation by linear α,ω -dihaloalkanes in acetonitrile (even with the addition of 5–10 vol% DMSO) is very slow at room temperature under the action of alkali metal carbonates as bases.^{8,10} However, the higher electrophilicity of

[†] NMR spectra were recorded on Bruker WP-200SY and AMX-400 spectrometers in $CDCl_3$ and $[^2H_6]DMSO$ solutions using residual proton signals of the deuterated solvents as an internal standard (¹H, ¹³C) and 85% H_3PO_4 (³¹P) as an external standard. IR spectra were recorded in KBr pellets on a Magna-IR750 Fourier spectrometer (Nicolet); resolution of 2 cm^{-1} ; 128 scans. Starting thiophosphoryl acetonitrile **1b** was obtained by the reaction of a corresponding phosphorylacetonitrile with the Lawesson reagent.¹² Hexakis(bromomethyl)benzene was obtained by hexamethylbenzene bromination¹³ and its characteristics were consistent with published data.

Synthesis of 2,5,8-tris(diphenylthiophosphoryl)-2,3,4,5,6,7,8,9-octahydro-1H-cyclopent[e]-*asym*-indacene-2,5,8-tricarbonitriles 2a,b: A mixture of diphenylphosphorylacetonitrile **1a** or diphenylthiophosphorylacetonitrile **1b** (3 equiv., 4.15 mmol), K_2CO_3 (12 equiv., 2.3 g, 16.6 mmol) or Cs_2CO_3 (12 equiv., 5.4 g, 16.6 mmol) and hexakis(bromomethyl)benzene (1 equiv., 0.88 g, 1.38 mmol) in the mixed solvent MeCN–DMSO (95:5) (40 ml) was stirred at ambient temperature for 15–18 h (K_2CO_3) or 7–9 h (Cs_2CO_3). The reaction was monitored by ³¹P NMR spectroscopy. After completion of the reaction, the mixture was diluted with water (30 cm^3) and extracted with CH_2Cl_2 (3×50 cm^3). The combined organic layers were washed with water (2×30 cm^3), dried with $MgSO_4$ and evaporated to dryness. The residue was a DMSO solvate of crude product **1** (93–96% according to ³¹P NMR) with the molar ratio of DMSO to **1** equal to 1:2. The product was crystallised from benzene–EtOH and dried in a Fisher gun (5 h, 98 °C). The purified compounds gave satisfactory elemental analyses.

Selected data for 2a: yield 74–85% (depending on the base used, according to ³¹P NMR), 54–59% (after isolation as a DMSO solvate), 42–46% (after recrystallization); mp 290 °C (decomp., 0.5DMSO solvate), 340 °C (decomp). ³¹P-{¹H} NMR ($CDCl_3$) δ : 28.98 (one non-equivalent phosphorus atom in *cis-trans* **2a**), 28.76 (two phosphorus atoms in *cis-trans* **2a** + signal of the *cis-cis* isomer **2a**); ($[^2H_6]DMSO$) δ : 31.37, 31.25 (in a ratio of 2:1, *cis-trans* **2a**); 31.22 (*cis-cis* **2a**). ¹H NMR ($CDCl_3$) δ : 3.04–3.13 (m, 6H, CH_2 , *trans* to P=O), 3.61–3.87 (m, 6H, CH_2 , *cis* to P=O), 7.31–7.58 (m, 12H, *m*-PhP), 7.61–7.65 (m, 6H, *p*-PhP), 7.96–8.02 (m, 12H, *o*-PhP). ¹³C NMR ($CDCl_3$) δ : 38.28, 38.31, 38.29 (br., CH_2), 42.68 (d, one C–CN, ¹ J_{PC} 67.5 Hz, *cis-trans*), 42.55 (d, C–CN, ¹ J_{PC} 68.1 Hz, *cis-cis*), 42.31 (d, two C–CN, ¹ J_{PC} 67.5 Hz, *cis-trans*), 122.20 (br. s., CN), 128.88 (d, *m*-PhP, ³ J_{PC} 12.1 Hz), 128.92 (d, C–P in PhP, ¹ J_{PC} 101.1 Hz), 131.78 (d, *o*-PhP, ² J_{PC} 8.9 Hz), 132.94 (s, *p*-PhP), 134.34, 134.40 (C–Ar of the core benzene ring). IR (KBr, ν/cm^{-1}): 698, 726, 752, 1100, 1118, 1201 (P=O), 1438, 2230 (CN).

Selected data for 2b: yield 71–75% (according to ³¹P NMR), 53–58% after recrystallization; mp 340 °C (decomp.). ³¹P-{¹H} NMR ($CDCl_3$) δ : 55.40 (*cis-cis* **2b**), 55.26, 55.11 (in a ratio of 2:1, *cis-trans* isomer). ¹H NMR ($CDCl_3$) δ : 3.11–3.16 (m, 6H, CH_2 , *trans* to P=S), 3.82–3.95 (m, 6H, CH_2 , *cis* to P=S), 7.57–7.65 (m, 18H, *p,m*-PhP), 8.12 (dd, 12H, *o*-PhP, ³ J_{CH} 12.8 Hz, ³ J_{HH} 7.9 Hz). ¹³C NMR ($CDCl_3$) δ : 39.87 (br., CH_2), 44.60 (d, one C–CN, ¹ J_{PC} 50.3 Hz, *cis-trans*), 44.64 (d, C–CN, ¹ J_{PC} 50.8 Hz, *cis-cis*), 44.68 (d, two C–CN, ¹ J_{PC} 50.7 Hz, *cis-trans*), 122.30 (s, two CN, *cis-trans*), 122.36 (s, CN, *cis-cis*), 122.45 (s, two CN, *cis-trans*), 128.85 (d, *m*-PhP, ³ J_{PC} 12.5 Hz), 128.98 (d, C–P in PhP, ¹ J_{PC} 81.9 Hz), 132.34 (d, *o*-PhP, ² J_{PC} 9.9 Hz), 132.64 (br., *p*-PhP), 134.23, 134.16, 134.09 (br. s., C–Ar of the core benzene ring). IR (KBr, ν/cm^{-1}): 656, 691, 722, 749, 1099, 1436, 1481, 2228 (CN).



benzyl carbon atoms allowed us to carry out the reaction smoothly under the above conditions.

Compounds **2** are readily soluble in halogenated hydrocarbons, and they display extremely high thermal stability with practically the same decomposition point (340 °C, **2a,b**). The crude products were isolated from the reaction mixtures as solvates with the molar ratio DMSO:product **2** equal to 1:2 (according to ^1H NMR spectra). It is also noteworthy that compounds **2** readily form rather strong solvate complexes with other solvents such as benzene and toluene. Long heating under a vacuum is required for the decomposition of the complexes.

The structures of compounds **2a,b** were elucidated by IR and NMR (^1H , ^{31}P , ^{13}C) spectroscopy. Thus, three adjacent signals were observed in the ^{31}P NMR spectra of trindans **2a** ($[\text{D}_6]\text{DMSO}$, Figure 1) and **2b** (CDCl_3 , Figure 2).[‡] The integral intensity of one of the signals depends upon the nature of a base used in the synthesis. This signal is attributed to the corresponding *cis-cis* isomer possessing three equivalent phosphorus atoms with the same surrounding. Two other signals are detected in all cases with an intensity ratio of 2:1, and they correspond to two equivalent phosphorus atoms with identical surroundings and to the transoid phosphorus atom in the *cis-trans* isomer, respectively. Similarly, three doublet signals of the gem-disubstituted carbon atom of the cyclopentane ring are observed in ^{13}C NMR spectra. One of the doublets is attributed to this carbon atom in the *cis-cis* isomer while two other with the integral intensity ratio 2:1 belong to two equivalent carbon atoms in the *cis* position and a non-equivalent atom in the *trans* position of the second isomer. In ^1H NMR spectra, in addition to the signals of aromatic hydrogen atoms in phenyl substituents at the phosphorus atoms, two multiplets were assigned to methylene-group protons located in *trans*- [3.038–3.135 (**2a**), 3.108–3.163 (**2b**)], and *cis*- [3.609–3.886 (**2a**), 3.822–3.956 (**2b**)] positions with respect to thiophosphoryl groups.[§]

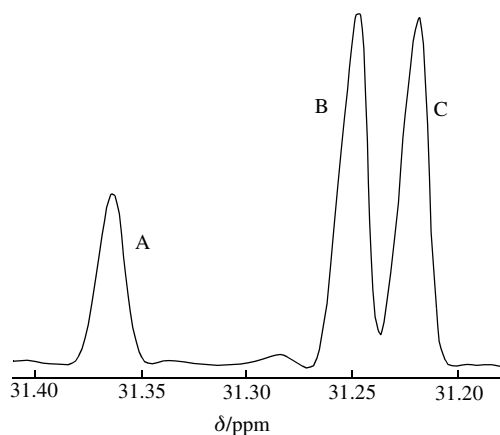


Figure 1 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum (in $[\text{D}_6]\text{DMSO}$) of trindane **2a** synthesised in the presence of Cs_2CO_3 . A is the signal corresponding to one non-equivalent phosphorus atom in the *cis-trans* isomer; B is the signal corresponding to two equivalent phosphorus atoms in the *cis-trans* isomer; C is the signal of phosphorus atoms in the *cis-cis* isomer.

[‡] Because of the overlapping of signals B and C in the ^{31}P NMR spectra of **2a** in CDCl_3 , two closely located signals are observed.

[§] The signals were assigned according to ref. 14.

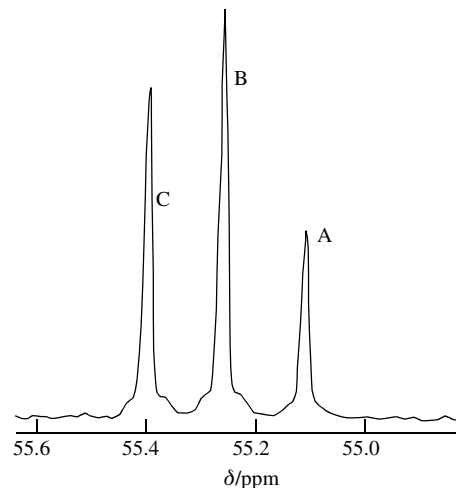


Figure 2 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum (in CDCl_3) of trindane **2b** synthesised in the presence of K_2CO_3 . A, B and C are specified in Figure 1.

Hence, according to the spectroscopic data, the products are formed as a mixture of two stereoisomers (*cis-cis* and *cis-trans*) in the ratios of 30:70 (K_2CO_3) and 40:60 (Cs_2CO_3) for **2a** and 35:65 (K_2CO_3) for **2b**. In other words, in all cases, the more thermodynamically stable and less sterically hindered *cis-trans* isomer is formed in a greater amount.

Note that our attempt to use 1,2,3,4-tetrakis(bromomethyl)-benzene in cycloalkylation to produce 2,7-bis(diphenylphosphoryl)- or 2,7-bis(diphenylthiophosphoryl)-1,2,3,6,7,8-hexahydro-*asym*-indacene-2,7-carbonitriles was unsuccessful and resulted in the formation of a complex mixture of low-molecular-weight and polymeric alkylation products.

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