Synthesis and characterization of polychlorinated naphthalenes. VI. PCNs 39, 41, 60, 61 and 62

Vladimir A Nikiforov[1]

[1]St.petersburg State University, Dept. Of Chemistry

Introduction

In a series of presentations at DIOXIN symposia we have reported synthesis and characterization of a large number of polychloronaphthalenes[1-5]. By the end of the last century only 10 congeners remained unknown or inadequately characterized – PCNs 2, 29, 39, 41, 45, 51, 58, 60, 61, 62. In particular, no melting point was reported for these 10 congeners, except PCN 2. This congener (2-chloronaphthalene) is the only liquid at ambient temperatures, with reported melting point from -17 ^{o}C to -2.3^{o}C.

Our research is directed towards synthesis of all 75 PCN congeners and present work describes synthesis and properties of the following congeners

PCN 39 – 1,2,6,7-TeCN

PCN 41 – 1,2,7,8-TeCN

PCN 60 – 1,2,4,6,7-PeCN

PCN 61 – 1,2,4,6,8-PeCN

PCN 62 – 1,2,4,7,8-PeCN

Materials and Methods

Starting PCN congeners were previously synthesized in our laboratory [1-6]. Nitration was carried out with equivalent amount of NO_2BF_4 in sulfolane at ambient temperature [1,4]. Chlorosulfonation was carried out in excess of neat HSO_3Cl. Substitution of nitro- and chlorosulfonyl groups was achieved in boiling C_5Cl_6 [4,7]. For hydrodechlorination Cu in boiling acetic acid was employed [5,6].

Nitro-PCNs and PCN-sulfonylchlorides were purified by crystallization from ethanol. PCNs were purified by chromatography on silicagel column with hexane as eluent; then crystallized from MeOH/CH_2Cl_2. All chemicals and reagents were used as received.

Course of reactions, separations and purifications and purities of products were controlled by GC/ECD. GC conditions were as follows : GC-Varian3700, inj. – Gerstel split/splitless at 250^{o}C, column – DB-5(app. 50m), Det. – ECD(at 300^{o}C), carrier gas – nitrogen, make-up – nitrogen. Pr.: 160 ^{o}C(2 min) - 20 ^{o}C/min - 280 ^{o}C(10 min) Purge 1.00-1.90 min. Structures were established by NMR.

Results and Discussion

Structures of “missing” PCN congeners are given below (Fig. 1). Interestingly, one mono-CN, four tetraCNs and 5 penta-CNs have not been either reported at all or incompletely characterized by the beginning of our century.

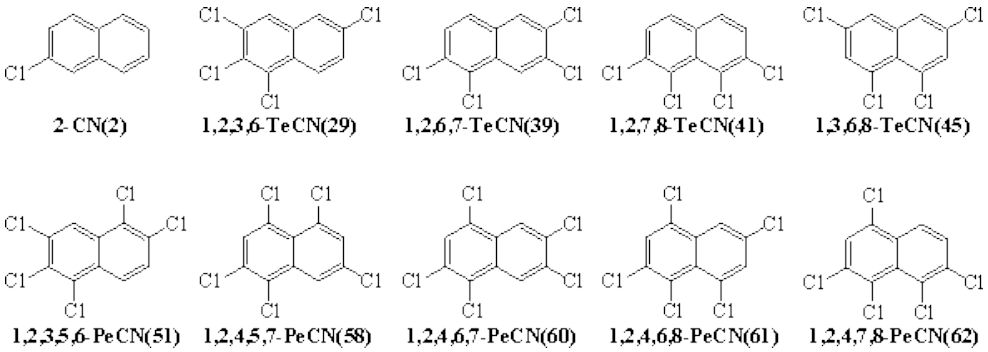
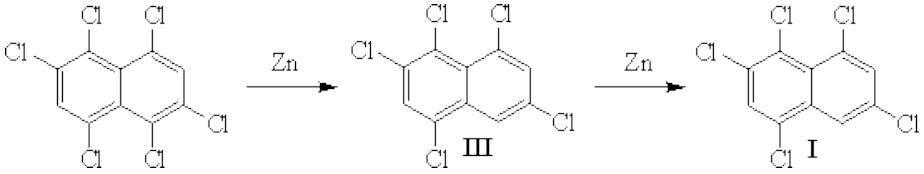


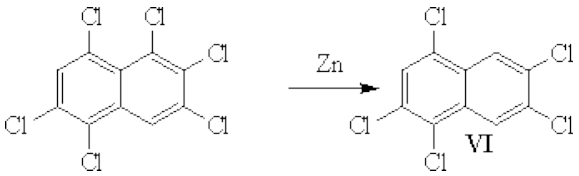
Figure 1. Structures of unknown or incompletely characterized PCN congeners. In brackets – PCN numbers.

Five of the ten missing congeners were prepared according to the scheme on Fig. 2.

For confirmation purposes 1,2,4,5,7-PeCN(**III**) was also obtained by alternative synthetic route - as intermediate by reduction of 1,2,4,5,7,8-HxCN with Zn [5,6].



1,2,4,6,7-PeCN(**VI**) was similarly prepared in minuscule amount from 1,2,3,5,7,8-HxCN [6].



Nitration of 1,2,4,7-TeCN(**IV**) gave a mixture of products, two were isolated in pure state by chromatography on silicagel with hexane as eluent – 3-nitro-1,2,4,7-TeCN(**VII**) and 8-nitro-1,2,4,7-TeCN(**VIII**). The latter was converted to 1,2,4,7,8-PeCN(**IX**). This compound was also obtained by alternative route **XIII**→ **X** → **XI**→ **XII** → **IX**.

Hydrodechlorination of 1,2,3,7,8-PeCN(**XIV**) with Zn yields target 1,2,6,7-TeCN(**XV**), ca. 80% and side product 1,2,3,7-TeCN, ca 20% [5,6]. The mixture was separated on silicagel with hexane as eluent.

Melting points, GC retention times and ^{1}H NMR chemical shifts are summarized in Table 1.

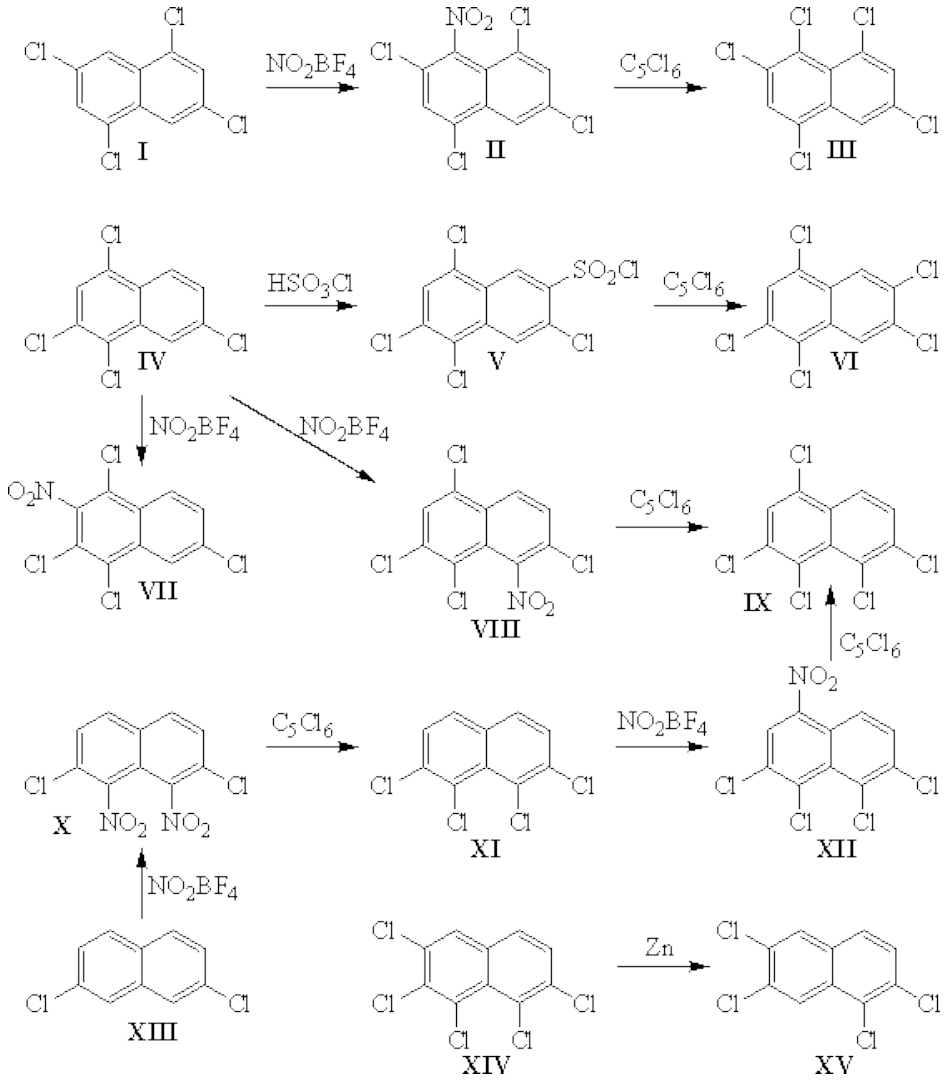


Figure 2. Synthesis of 1,2,6,7-TeCN(**XV**), 1,2,7,8-TeCN(**XI**), 1,2,4,6,7-PeCN(**VI**), 1,2,4,6,8-PeCN(**III**) and 1,2,4,7,8-PeCN(**IX**).

Table 1. Melting points, GC retention times(RT) and ^{1}H NMR chemical shifts of PCNs and related compounds (compound numbers – Fig. 2)

Compound number	RT	Melting point	^{1}H NMR chemical shifts, d(ppm)						
			H-2	H-3	H-4	H-5	H-6	H-7	H-8
I	6.52,2	176	7.63d	-	8.14d	-	7.63d	-	8.14d
III	8.30,4	155.5	-	4.76s	-	8.26d	-	7.74d	-
IV	7.08,3	143	-	7.64s	-	8.18d	7.59dd	-	8.29d
V	-	-	-	7.83s	-	9.10s	-	-	8.56s
VI	8.18,1	130.2	-	7.66s	-	8.41s	-	-	8.35s
VII	-	-	-	-	-	8.31d	7.74dd	-	8.36d
VIII	9.32,8	109	-	7.83s	-	8.41d	7.71d	-	-
IX	8.49,6	103.4	-	7.75s	-	8.20d	7.69d	-	-
X	10.26,8	256	-	7.75d	8.05d	8.05d	7.75d	-	-
XI	8.07,2	128.1	-	7.60d	7.68d	7.68d	7.60d	-	-
XII	9.33,0	-							

XIV	9.18,7	117	-	-	7.87s	7.59s	7.59s	-	-
XV	7.36,8	156.9	-	7.53d	7.61d	7.94s	-	-	8.39s

Thus we have half-finished the remaining work on synthesis and characterization of all 75 PCN congeners. Synthesis of 1,2,3,6-TeCN, 1,3,6,8-TeCN, 1,2,3,5,6-PeCN and 1,2,4,5,7-PeCN is in progress.

Acknowledgement

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