

Isolation and Structure Elucidation of Polychlorodihydrocamphenes - Potential Constituents of Toxaphene Residues.

Vyacheslav G. Tribulovich¹, Vladimir A. Nikiforov², Sergei Bolshakov¹

¹St.Petersburg University, Department of Chemistry, 199034, Universitetskaya nab., 7/9, St.Petersburg, Russia

²St.Petersburg University, Institute of Chemistry, 198904, Universitetsky pr. 2, St.Petersburg, Stary Peterhof, Russia

Introduction

It was believed for many years, that Toxaphene mixture contains predominantly Polychlorobornanes and Polychlorobornenes, plus some Polychlorobornadienes¹). The only evidence of the presence of other polychloroterpenes was isolation of 2-exo,3-exo,6-exo,8,9,10,10-Heptachlorodihydrocamphene²). In 1994 Parlar et.al. have first reported isolation and structure elucidation of a group of Polychlorocamphenes and indicated their environmental importance³).

However, there is no clear understanding of the mechanism of Polychlorocamphenes formation. Dechlorination of Bornanes with rearrangement to Camphenes, proposed by Parlar, is unlikely, because :

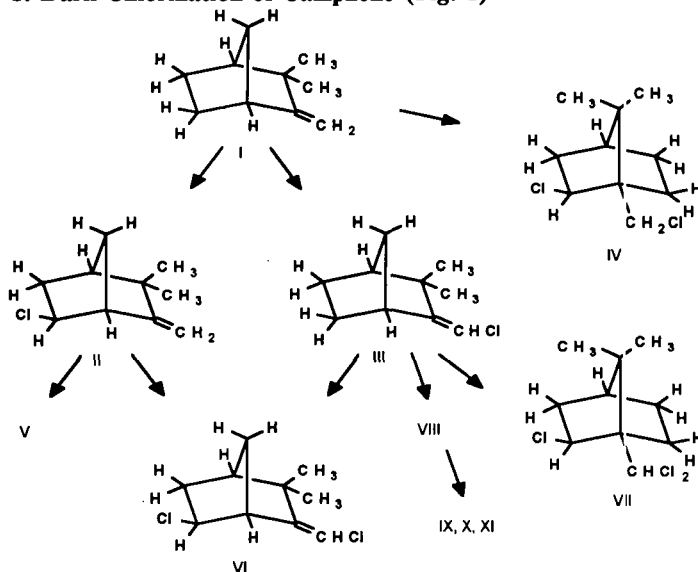
- Only for one out of five isolated polychlorocamphenes corresponding bornane precursor was isolated.
- This compound, 2-endo,3-exo,5-endo,6-exo,8,9,10,10-Octachlorobornane (hypothetical precursor of 2-exo,3-endo,7a,8b,9c,10a-Hexachlorocamphene) is quite stable under UV-irradiation and is one of the major components of CB-standard.
- Precursors of 3 out of five polychlorocamphenes should possess 2,2,3-endo,6-exo-tetrachlorosubstitution pattern of ring methylene groups (never observed)
- Polychlorocamphenes have never been detected among the products of chlorination of specially purified low chlorinated bornanes (2-exo,10-DiCB and 2-exo,10,10-TriCB)

It is likely, that polychlorocamphenes are formed from low chlorinated camphenes, the early products of chlorine addition to camphene.

The question of the origin of polychlorocamphenes is closely linked to the question of the source of pollution, so we have undertaken detailed investigation of chlorination of camphene in the absence of light, in an attempt to identify and isolate a compound with camphene skeleton, which undergoes free-radical chlorination without rearrangement.

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1. Dark Chlorination of Camphene (Fig. 1)



1) Chlorination of Camphene with insufficient amount of chlorine

Chlorination of Camphene with 0,1 eqv. of chlorine yields 3 major products :

6-exo-Chlorocamphene (II)

cis- and trans- 8-exo-Chlorocamphenes (III)

2,10-Dichlorobornane (IV)

The products were separated by rectification. IV does not react with chlorine without UV. Two other products were chlorinated separately.

2) Chlorination of 6-exo-Chlorocamphene

There are only two products :

x,x,x-Trichlorobornane (V)

cis- and trans- 6-exo,8-Dichlorocamphenes (VI)

The minor product, trichlorobornane V, remains unchanged with further addition of chlorine. Surprisingly, so does dichlorocamphene VI !

3) Chlorination of cis- and trans- 8-Dichlorocamphenes;

Initially, three products are formed :

2-exo,10,10-Trichlorobornane (VII)

cis- and trans- 6-exo,8-Dichlorocamphenes (VI)

x,x-Dichlorocamphene (VIII)

The first two compounds are stable, while the last produces under further chlorination three minor tri- to tetra- chloroderivatives IX, X and XI, which have not been studied.

4) Chlorination of Camphene with an excess of chlorine;

The following ratio of the products was found :

2-exo,10-Dichlorobornane (IV) - 57%

2-exo,10,10-Trichlorobornane (VII) - 26%

cis- and trans- 6-exo,8-Dichlorocamphenes (VI) - 7%

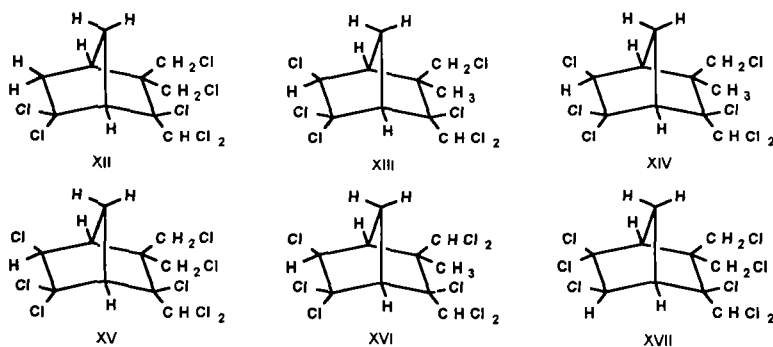
Other products - 10%

Thus, the third major product of the dark chlorination of camphene is a mixture of *cis*- and *trans*-6-*exo*,8-Dichlorocamphenes VI. It is well-known, that photochlorination of IV and VII yields mixtures of polychlorobornanes⁴). Naturally, the next step of our work was photochlorination of 6-*exo*,8-Dichlorocamphene, separation of a product mixture on a hexane/silicagel column and structure elucidation of individual congeners.

3. Photochlorination of *cis*- and *trans*-6-*exo*,8-Dichlorocamphenes

Chlorination to the average of 7-8 chlorine atoms in a molecule and separation in a usual manner⁴) allowed us to isolate a number of compounds in amounts of 20 - 200mg. Six of them were studied by NMR, and we can assign a structure of Polychlorodihydrocamphenes (Fig. 2), despite positions of methyl-, chloromethyl and dichloromethyl- groups, as well as of a remaining proton at 2-*endo* or 3-*endo*- position in compounds XIII - XVII are not finally determined.

Fig. 2. Structures of Polychlorodihydrocamphenes



¹H-spectra of isolated compounds differ from those of Polychlorobornanes dramatically.

All of them contain characteristic pattern :

-Singlet of H10 at 6,77-6,89ppm

-Two broad singlets of H1 and H4 at 3,49-3,73ppm and 2,43-2,97ppm respectively

-Two broad doublets of H7a and H7b(broader) at 2,28-2,49ppm and 2,67-2,70ppm respectively ($J = 12-13\text{Hz}$)

Such behaviour is in accordance to NMR spectra of Polychlorocamphenes³), however, ¹³C-spectra of compounds XIV-XVII unequivocally show an absence of double bonds; DEBT and proton-proton decoupling experiments for compounds XIV and XVI also are in accordance with the given structures.

GC retention times of compounds XII - XVII also confirm chlorination extent, corresponding to Dihydrocamphenes rather than to Camphenes, and are slightly longer, than those for Bornanes with the same number of Cl-atoms (Table 1).

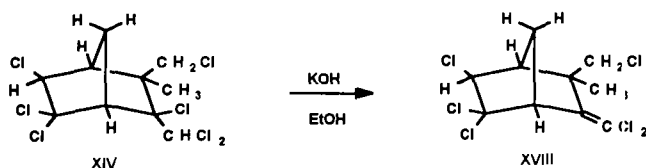
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Table 1. Retention times(RT,min) and retention indices(RI) of Polychlorodihydrocamphenes

Compound	RT	RI
XVII	14.84	1692
XIII	16.92	1812
XIV	17.38	1864
XII	18.11	1949
XVI	18.99	2050
XV	19.65	2069

Additionally, compound XIV was dehydrochlorinated to Hexachlorcamphene XVIII (Fig. 3). This is another confirmation of the proposed structures.

Fig. 3. Dehydrochlorination of Heptachlorodihydrocamphene XIV



Further NMR and GC/MS experiments, scheduled for the nearest future shall lead to the final elucidation of the structures.

Conclusions

- A mixture of cis- and trans- 6-exo-8-Dichlorocamphenes is found to be a possible precursor of Polychlorodihydrocamphenes in technical Toxaphene.
- A number of Polychlorodihydrocamphenes is isolated, structures of 6 congeners are elucidated in general.
- Chromatogram of a chlorination mixture of 6-exo,3-Dichlorocamphene consists of 15 significant peaks only. 6 Polychlorodihydrocamphenes XII-XVII represent about 50% of a mixture, and, together, may contribute up to 4% of Technical Toxaphene.

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