

CHROM. 9087

## Note

### Separation of inorganic isomers by thin-layer chromatography

#### VI. Isomers of the non-metals boron, phosphorus and silica

GEORGE B. KAUFFMAN, BARRY H. GUMP, BRIAN J. STEDJEE and RICHARD A. HOUGHTEN, Jr.

*Department of Chemistry, California State University, Fresno, Calif. 93740 (U.S.A.)*

(Received February 9th, 1976)

In previous papers in this series, we described the separation by thin-layer chromatography (TLC) on silica gel of square planar non-electrolytic geometric isomers of platinum(II)<sup>1</sup>, octahedral non-electrolytic and electrolytic geometric isomers of various metals<sup>2</sup>, square planar non-electrolytic and electrolytic geometric isomers of various metals<sup>3</sup>, ligand isomers of various coordination numbers<sup>4</sup>, and structural, linkage, geometric, and conformational isomers of various coordination numbers<sup>5</sup>. In the present paper we extend our TLC separations to include isomers of non-metals. Inasmuch as we demonstrated in our first article<sup>1</sup> that TLC separations can be carried out on a semiquantitative preparative scale (with *ca.* 200 mg of total mixtures), all the separations reported here are strictly qualitative. In addition to using mixtures prepared from pure isomers, we also applied the method to materials that should theoretically exist in more than one isomeric form.

#### EXPERIMENTAL

Isomer samples were kindly provided by the persons listed alphabetically under Acknowledgements (designated by initials in Table I). All solvents were C.P. or reagent grade. Generous samples of the adsorbents used, SilicAR® TLC-7F and TLC-7G, were provided by Mallinckrodt (St. Louis, Mo., U.S.A.). Microscope slides (75 × 25 mm) were used for plates and were developed by the ascending technique. Iodine vapor was used for visualizing all samples except for sample 11, which was detected by ultraviolet (UV) light. Samples 6-10 may also be detected by UV light. Separated isomers were identified by comparison with  $R_F$  values obtained for the pure isomers when available or by mixed melting point measurements or other characterization techniques. Further details are given in previous articles<sup>1,2</sup>.

#### RESULTS AND DISCUSSION

The results obtained are summarized in Table I.  $R_F$  values were reproducible within  $\pm 0.03$ . Although many developing solvents and mixtures were evaluated, only the most successful combination, *i.e.*, those resulting in maximum differences

TABLE I  
THIN-LAYER CHROMATOGRAPHY OF NON-METAL ISOMERS

No.	Isomer	Source	Developing solvent	$R_F$	$\Delta R_F$	Type of separation
<i>Boron compounds</i>						
<i>Trimeric alkylaminoboranes or cyclotriborazines</i>						
1	(CH <sub>3</sub> ·NH·BH <sub>2</sub> ) <sub>3</sub> (a) <i>cis</i> (white) (b) <i>trans</i> (white)	M.P.B. <sup>6,7</sup>	CH <sub>2</sub> Cl <sub>2</sub>	0.53* (a) 0.78* (b)	0.25	Complete
2	(C <sub>2</sub> H <sub>5</sub> ·NH·BH <sub>2</sub> ) <sub>3</sub> (a) <i>cis</i> (white) (b) <i>trans</i> (containing. ca. 5% C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> ·BH <sub>3</sub> impurity) (white)	M.P.B. <sup>6,7</sup>	CH <sub>2</sub> Cl <sub>2</sub>	0.65* (a) 0.80* (b)	0.15	Complete
<i>Carboranes</i>						
3	B <sub>10</sub> H <sub>10</sub> C <sub>2</sub> H <sub>2</sub> , Carborane (Dicarba- <i>closo</i> -dodecaborane (12))  (a) <i>o</i> -carborane <sup>8,9,12</sup> (1,2-dicarba-) (white) (b) <i>m</i> -carborane or neocarbo- rane <sup>10-12</sup> (1,7-dicarba-) (white)	H.A.S. and T.L.H. <sup>8-12</sup>	Dissolved in C <sub>6</sub> H <sub>6</sub> , developed in CCl <sub>4</sub>  Dissolved in C <sub>6</sub> H <sub>6</sub> , developed in (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	0.60 (a) 0.85 (b)  0.65 (a) 0.95 (b)	0.25  0.30	Complete  Complete
4	B <sub>10</sub> H <sub>8</sub> Br <sub>2</sub> C <sub>2</sub> H <sub>2</sub> , <sup>13,14</sup> B-Dibromocarborane (a) 9,10-dibromo- <i>ortho</i> (white) (b) 9,10-dibromo- <i>meta</i> (white)	H.A.S. and T.L.H.	Dissolved in C <sub>6</sub> H <sub>6</sub> , developed in (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	0.83 (a) 0.95 (b)	0.12	Complete
<i>Phosphorus compounds</i>						
<i>Phosphazene tetramers</i>						
5	P <sub>4</sub> N <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>6</sub> [N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> , 2,6-bis- (dimethylamino)hexaphenyl- cyclophosphazene tetramer; presumed mixture of <i>cis</i> and <i>trans</i> isomers (white)	C.M.S. <sup>15</sup>	Dissolved in CHCl <sub>3</sub> , developed in C <sub>6</sub> H <sub>6</sub> Dissolved in CHCl <sub>3</sub> , developed in (CH <sub>3</sub> ) <sub>2</sub> CO- CCl <sub>4</sub> (1:4)	0.00** 0.38** 0.00** 0.92**	0.38  0.92	Complete?  Complete?
6	P <sub>4</sub> N <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> (OC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub> , dichlorodiphenylbis(phenoxy)- cyclophosphazene tetramer; two separate isomers (I) and (II) (white), of the following structure	L.W.B. <sup>16</sup>				
			Dissolved in THF, developed in CH <sub>2</sub> Cl <sub>2</sub> Dissolved in THF, developed in CHCl <sub>3</sub>	0.85 (II) 0.95 (I) 0.70 (II) 0.80 (I)	0.10 0.10	Partial Partial
	in which 2 of the R groups are C <sub>6</sub> H <sub>5</sub> O and the other 2 are Cl, but the specific structures are unknown					

(Continued on p. 450)

TABLE I (continued)

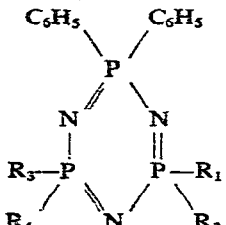
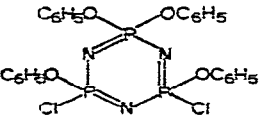
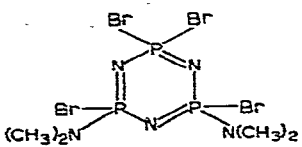
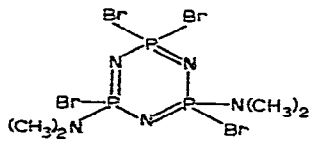
No.	Isomer	Source	Developing solvent	$R_F$	$\Delta R_F$	Type of separation
7	$P_4N_4(C_6H_5)_4Cl_4$ , tetrachlorotetra-phenylcyclophosphazene, tetramer (structure of sample 6 in which all 4 R groups are Cl); presumably a mixture of several <i>cis-trans</i> isomers (white)	L.W.B. <sup>16,17</sup>	Dissolved in THF, developed in $CCl_4$	0.36** 0.80**	0.44	Complete
<i>Phosphazene trimers</i>						
8	$P_3N_3(C_6H_5)_2(OC_6H_5)_2Cl_2$ , dichlorodiphenylbis(phenoxy)-cyclophosphazene trimer; presumably a mixture (white) of isomers of the structure	I.I.B. <sup>18,19</sup>	Dissolved in THF, developed in $CHCl_3$	0.73** (weak) 0.80** 0.92**	—	Complete
			Dissolved in THF, developed in $CCl_4$	0.24** 0.68**	0.44	Complete
	in which 2 of the R groups are $C_6H_5O$ and the other 2 are Cl, but the specific structures are unknown					
9	$P_3N_3(C_6H_5)_2Cl_2[N(CH_3)_2]_2$ , dichlorodiphenylbis(methylamino)-cyclophosphazene trimer; a mixture of isomers each with the structure of sample 8; for one, $R_1$ and $R_3$ are Cl, and $R_2$ and $R_4$ are $N(CH_3)_2$ ; for the other, $R_1$ and $R_4$ are Cl, and $R_2$ and $R_3$ are $N(CH_3)_2$ (white)	I.I.B. <sup>18</sup>	Dissolved in THF, developed in $CHCl_3$	0.00** 0.74** 0.90**	—	Complete
			Dissolved in THF, developed in $CCl_4$	0.00** 0.23** 0.72*	—	Complete
10	$P_3N_3(OC_6H_5)_4Cl_2$ , dichlorotetrakis-(phenoxy)cyclophosphazene trimer; presumably a mixture (colorless oil) of <i>cis-trans</i> isomers of the structure	I.I.B. <sup>18</sup>	Dissolved in THF, developed in $CCl_4$	0.24** 0.31** 0.73*	—	Complete
						
11	$P_3N_3F_4(C_6H_5)_2$ , diphenylphosphazene fluoride trimer (a) 1,1- or <i>gem</i> -diphenyl <sup>20-22</sup> (white)	T.M. <sup>20-22</sup>	$CHCl_3$ $CCl_4$	0.23 (b) 0.35 (a) 0.27 (b) 0.37 (a)	0.10	Partial Partial

TABLE I (continued)

No.	Isomer	Source	Developing solvent	$R_F$	$\Delta R_F$	Type of separation	
	(b) <i>cis</i> -1,3-diphenyl <sup>21,22</sup> (white)		$\text{CHCl}_3$	0.24 (c) 0.32 (a)	0.08	Partial	
	(c) <i>trans</i> -1,3-diphenyl <sup>21,22</sup> (white)		$n\text{-C}_5\text{H}_{12}\text{-CHCl}_3$ (1:1)	0.14 (b) 0.18 (c) 0.37 (a)	—	Partial	
12	$\text{P}_3\text{N}_3\text{Br}_4[\text{N}(\text{CH}_3)_2]_2$ , bis(dimethylamino)phosphazene bromide trimer	E.S. <sup>23</sup>	Dissolved in $(\text{CH}_3)_2\text{CO}$ , developed in $(\text{CH}_3)_2\text{CO}$	0.74 (b) 0.94 (a)	0.20	Partial	
			(a) <i>cis</i> (yellow-white)	Dissolved in $(\text{CH}_3)_2\text{CO}$ , developed in $\text{CH}_3\text{OH}$	0.74 (b) 0.90 (a)	0.16	Partial
			(b) <i>trans</i> (white)				

\* Minor spots, probably due to impurities, were observed on the chromatograms.

\*\* Since the sample provided was a mixture and since the pure isomers were not available for reference, it is not certain which spot is due to which isomer.

between  $R_F$  values and minimum tailing, are shown. Of the separations shown in Table I, all are complete except for those of samples 6, 11, and 12. For sample 5, unless the spot at the origin was an isomer rather than an impurity, no separation occurred.

In addition to the isomers shown in Table I, separations were attempted with the following isomers but were unsuccessful for the reasons cited. Carboranes:  $\text{B}_{10}\text{H}_{10}\text{C}_2(\text{COOH})_2$  (Carborane dicarboxylic acids), *ortho* (white) and *meta* (white) (H.A.S. and T.L.H.<sup>24</sup>), similar  $R_F$  values in all solvent systems used; phosphazene tetramers:  $\text{P}_4\text{N}_4(\text{C}_6\text{H}_5)_4\text{Cl}_4$  (1,3,5,7-tetraphenyl-2,4,6,8-tetrachlorocyclotetraphosphazene), *cis* (white),  $\beta$ -*trans* (white) (B.G.<sup>25</sup>),  $R_F$  values of both isomers very similar in all solvents and solvent mixtures used; N-substituted cyclotrisilazanes and N-substituted siloxazanes:  $[\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{N}(\text{CH}_3)]_3$ , *cis*- and *trans*-hexamethyl-2,4,6-triphenylcyclotrisilazane;  $[\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_2\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{N}(\text{CH}_3)$  (white powders), *cis*-1,2,4,6-tetramethyl-2,4,6-triphenyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (white powder) and the isomeric mixture from which it was obtained (colorless oil);  $[\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{OSi}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{N}(\text{CH}_3)]_2$ , *cis*-1,2,4,5,6,8-hexamethyl-2,4,6,8-tetraphenyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (white powder) and the isomeric mixture from which it was obtained (colorless oil) (L.W.B.<sup>26,27</sup>), generally no movement in any solvents, occasionally slight streaks obtained.

## CONCLUSIONS

In this paper we have employed TLC to separate geometric isomers of classes of compounds that have been the subject of much current research interest, the planar, three-membered cyclic borazines, icosahedral carboranes<sup>28-30</sup>, and planar three-membered and four-membered cyclic phosphazenes<sup>31,32</sup>. Our attempts to separate cyclic silazanes and siloxazanes, however, were unsuccessful. More than has been the case with isomers of metals, column chromatography<sup>33-37</sup> and TLC<sup>34,35</sup> have been applied to studies of isomers of non-metals—to follow the course of reactions, establish isomeric purity, and, in conjunction with other evidence, to establish isomeric configurations<sup>34,36</sup>.

The advantages of TLC in the separation of inorganic isomers have been discussed in previous articles<sup>1,2</sup>. In column chromatography, with only a few exceptions, the *trans* isomer is more mobile than the *cis* isomer and is therefore eluted first<sup>38</sup>. In TLC, on the other hand, while we and others<sup>34,38</sup> have likewise found that generally the *trans* isomer is more mobile, *i.e.*,  $R_F \text{ trans} > R_F \text{ cis}$ , exceptions to this general rule appear to be more numerous. (In the present paper, samples 11 and 12 exhibited this behavior; because samples of the pure isomers were unavailable for samples 5-10, their TLC sequences could not be determined). Therefore, while TLC behavior may have some value in proof of configuration, it should be used with more caution than column chromatographic elution sequence and should always be supplemented by other data.

## ACKNOWLEDGEMENTS

We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 1152-B), the National Science Foundation (Undergraduate Research Participation Program Grants GY 2607 and GY 9916), and the California State University, Fresno Research Committee for support of this research. We also wish to thank Richard A. Albers, Al Gwilliams, Samuel E. Hudson, Dennis W. Janzen, Robert K. Masters, Eicke Olsen, Philip Posson, and Paul Vartanian for experimental assistance and the following persons, listed in alphabetical order, for kindly providing experimental samples of isomers: I. I. Bezman, Lawrence W. Breed, Michael P. Brown, Bernard Grushkin, Theodore L. Heying, Therald Moeller, Hansjürgen A. Schroeder, Clay M. Sharts, and E. Steger.

## REFERENCES

- 1 G. B. Kauffman and B. W. Benson, *Inorg. Chem.*, 6 (1967) 411.
- 2 G. B. Kauffman, B. H. Gump and B. J. Stedjee, *J. Chromatogr.*, 117 (1976) 455.
- 3 G. B. Kauffman, B. H. Gump and B. J. Stedjee, *J. Chromatogr.*, 118 (1976) 433.
- 4 G. B. Kauffman, B. H. Gump and B. J. Stedjee, *J. Chromatogr.*, 121 (1976) 138.
- 5 G. B. Kauffman, B. H. Gump and B. J. Stedjee, *J. Chromatogr.*, 121 (1976) 395.
- 6 M. P. Brown, R. W. Heseltine and D. W. Johnson, *J. Chem. Soc., A*, (1967) 597.
- 7 M. P. Brown, R. W. Heseltine and L. H. Sutcliffe, *J. Chem. Soc., A*, (1968) 612.
- 8 T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak and J. W. Szymanski, *Inorg. Chem.*, 2 (1963) 1089.
- 9 M. M. Fein, J. Babinski, N. Mayes, N. Schwartz and M. S. Cohen, *Inorg. Chem.*, 2 (1963) 1111.
- 10 D. Grafstein and J. Dvorak, *Inorg. Chem.*, 2 (1963) 1128.

- 11 H. Schroeder and G. D. Vickers, *Inorg. Chem.*, 2 (1963) 1317.
- 12 A. W. Laubengayer and W. R. Rysz, *Inorg. Chem.*, 4 (1965) 1513.
- 13 H. D. Smith, T. A. Knowles and H. Schroeder, *Inorg. Chem.*, 4 (1965) 107.
- 14 R. Maruca, H. Schroeder and A. W. Laubengayer, *Inorg. Chem.*, 6 (1967) 572.
- 15 C. M. Sharts, A. J. Bilbo and D. R. Gentry, *Inorg. Chem.*, 5 (1966) 2140.
- 16 *Chem. Eng. News*, (June 28, 1965) 42.
- 17 M. Biddlestone and R. A. Shaw, *Chem. Commun.*, 11 (1965) 205.
- 18 C. T. Ford, F. E. Dickson and I. I. Bezman, *Inorg. Chem.*, 3 (1964) 177.
- 19 C. T. Ford, J. M. Barr, F. E. Dickson and I. I. Bezman, *Inorg. Chem.*, 5 (1966) 351.
- 20 C. W. Allen, J. B. Faught, T. Moeller and I. C. Paul, *Inorg. Chem.*, 8 (1969) 1719.
- 21 C. W. Allen and T. Moeller, *Inorg. Chem.*, 7 (1968) 2177.
- 22 C. W. Allen, F. Y. Tsang and T. Moeller, *Inorg. Chem.*, 7 (1968) 2183.
- 23 R. Stahlberg and E. Steger, *J. Inorg. Nucl. Chem.*, 29 (1967) 961.
- 24 *Carborane Compounds*, Product Data and Chemistry, Olin Chemicals, Stamford, Conn.
- 25 B. Grushkin, A. J. Berlin, J. L. McCianahan and R. G. Rice, *Inorg. Chem.*, 5 (1966) 172.
- 26 L. W. Breed and R. L. Elliott, *Inorg. Chem.*, 3 (1964) 1622.
- 27 R. W. Elliott and L. W. Breed, *Inorg. Chem.*, 4 (1965) 1455.
- 28 E. L. Muettterties and W. H. Knoth, *Chem. Eng. News*, (May 9, 1966) 88.
- 29 W. N. Lipscomb, *Science*, 153 (1966) 373.
- 30 M. F. Hawthorne, *Endeavour*, 25 (1966) 146.
- 31 H. R. Allcock, *Chem. Eng. News*, (April 22, 1968) 68.
- 32 R. A. Shaw, *Endeavour*, 27 (1968) 74.
- 33 R. A. Shaw and C. Stratton, *J. Chem. Soc., London*, (1962) 5004.
- 34 R. Keat and R. A. Shaw, *J. Chem. Soc., London*, (1965) 2215.
- 35 R. Keat and R. A. Shaw, *J. Chem. Soc., A*, (1966) 908.
- 36 E. T. McBee, K. Okuhara and C. J. Morton, *Inorg. Chem.*, 5 (1966) 450.
- 37 J. F. Sieckhaus, N. S. Semenuk, T. A. Knowles and H. Schroeder, *Abstracts of Papers Presented at the 155th National Meeting, American Chemical Society, San Francisco, April 1-5, 1968*, Abstract M-208.
- 38 L. F. Druding and G. B. Kauffman, *Coord. Chem. Rev.*, 3 (1968) 409.