Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A Simple Synthesis of Deuterated 1.2.4.5 Tetrachlorobenzene

Herbert Zimmermann [a]

[a] Department of Chemistry, University of California Berkeley, California, 94720, USA

To cite this article: Herbert Zimmermann (1978): A Simple Synthesis of Deuterated 1.2.4.5 Tetrachlorobenzene, Molecular Crystals and Liquid Crystals, 49:1, 1-5

To link to this article: http://dx.doi.org/10.1080/00268947808070318

Mol. Cryst. Liq. Cryst. Vol. 49 (Letters), pp. 1-5

Printed in the United States of America

A SIMPLE SYNTHESIS OF DEUTERATED 1.2.4.5 TETRACHLOROBENZENE

HERBERT ZIMMERMANN*

Department of Chemistry
University of California
Berkeley, California 94720 USA

(Submitted for publication June 19, 1978)

Single crystals of 1.2.4.5-tetrachlorobenzene (TCB) are particularly interesting because of their basically one-dimensional exciton transport system.[1] Deuterated TCB-d_2 was used as single crystals to study shallow traps in TCB by optical, EPR and Optical Detection of Magnetic Resonance (ODMR) experiments.[2-5] TCB is the first substance where both zero-field and high-field ODMR of free excitons can be observed.[6] Therefore, there is a considerable interest to have a simple procedure to prepare the deuterated starting material TCB with high chemical and isotopic purity.

---

* permanent address:

Max-Planck-Institut
Abteilung für Molekulare Physik
Jahn-Straße 29
6900 Heidelberg, Federal Republic of Germany

Polychlorinated benzenes undergo an exchange with deuteriumsulfate, but particularly in the case of symmetrical tetrachlorobenzene (TCB) there is a simultaneous sulphonation at the required temperature of 150° C as reported by Leitch et al.[7]

In this study an easy and fast exchange with sodiumethoxide in ethanole-OD with high chemical yield and high chemical and isotopic purity is reported.

A kinetic investigation[8] of a nucleophilic displacement in the reaction of 1.2.4.5 TCB with sodiumethoxide in absolute ethanole was made at 180° C in an autoclave. The reaction products were 2.4.5-trichlorophenetole, 2.4.5-trichlorophenole and 1.3-diethoxy-4.6-dichlorobenzene. This reaction does not occur at reflux conditions in an Et-OD solution mixed with benzene. The two hydrogens in 1.2.4.5 TCB show a remarkable acidity and therefore a solution of sodiumethoxide in ethanole-OD can be used as a very efficient hydrogen deuterium exchange source.

After the first exchange the isotopic purity was determined by mass-spectroscopy, found ≈ 90 % TCB-d_2 and ≈ 10 % TCB-d_1. After a second exchange TCB was completely deuterated. No significant side-reactions were observed. With the same method and under similar conditions also 1.2.4.5-tetrabromobenzene-d_2 was synthesize

The deuterated TCB can also be recommended as high temperature solvent (mp = 138 - 140° C) for NMR-measurements. The thermal stability and its solubility properties are excellent. Traces of the protonated material show a singlet at 7.67 ppm (ref. cyclosilane). At 19000 scans, 200° C with a 360 MHz spectrometer, there were no additionally detectable hydrogen-containing impurities.

EXPERIMENTAL PART

1.2.4.5-tetrachlorobenzene-d_2

1.26 gr (0.055 m) sodium was added slowly to 46 gr (1 m) ethanole-OD (99.5 % Aldrich Chem.). After the sodium was dissolved, the solution was mixed with 30 ml benzene (stored over sodium) to increase the solubility of TCB and to prevent side-reactions. To this stirred mixture 7 gr (0.032 m) of 1.2.4.5 TCB (FLUKA, purum) were added and refluxed for 12 hours. The solution was cooled and the resulting crystallized deuterated TCB filtered off. This product was used to exchange a second time under the same conditions and yielded 5.1 gr (71 %) TCB-d_2 $\approx$ 99 % after sublimation under reduced pressure. m.p. 138 - 140° C.

As already found by Güttler et al.[9] the commercial grade TCB, even after extensive zone refining, contains impurities, mainly trichlorobenzene and tetrachlorobenzene-isomers detectable by gas-chromatography (GLC). The deuterated TCB was analysed by GLC after 100 zone-refining cycles. (Carbowax 20 M, 100° C carrier gas = N_2FID):

solvent	$5 \cdot 10^{-5}$	Mol/Mol
monochlorobenzene	$3 \cdot 10^{-5}$	" "
dichlorobenzene	$1 \cdot 10^{-5}$	" "
1.3.5 trichlorobenzene	$1.5 \cdot 10^{-4}$	" "
1.2.4+1.2.3 trichlorobenzene	$3 \cdot 10^{-4}$	" "
1.2.3.4 tetrachlorobenzene	$3.5 \cdot 10^{-4}$	" "

No detectable amounts of penta and hexachlorobenzene

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Miss Gudrun Pampel, University of Stuttgart, for the GLC measurements.

REFERENCES

1. A.H. Francis and C.B. Harris, Chem. Phys. Lett. 9, 181 (1971).

   D.M. Burland, D.E. Cooper, M.D. Fayer and C.R. Gochanour, Chem. Phys. Lett. 52, 279 (1977).
2. M.D. Fayer and C.B. Harris, Phys. Rev. B 9, 748 (1974).
3. M.T. Lewellyn, A.H. Zewail and C.B. Harris, J. Chem. Phys. 63, 3687 (1975).
4. M.D. Fayer and C.B. Harris, Chem. Phys. Lett. 25, 149 (1974).
5. A.H. Zewail and C.B. Harris, Phys. Rev. B 11, 952 (1975).
6. J. Ziegler and H.C. Wolf, Chem. Phys. 29, 209-217 (1978).

7. R.N. Renaud, D. Kovachic and L.C. Leitch, Can. J. Chem. 39, 21 (1961).

8. S.M. Shein and V.A. Ignatov, Zh. Obshch. Khim. 38(8), 2645-50 (1963).

9. W. Güttler, J.U. von Schütz and H.C. Wolf, Chem. Phys. 24, 159-165 (1977).

W. Güttler, Thesis 1976 Stuttgart.